Physical Chemistry Part 2

CHAPTER 5

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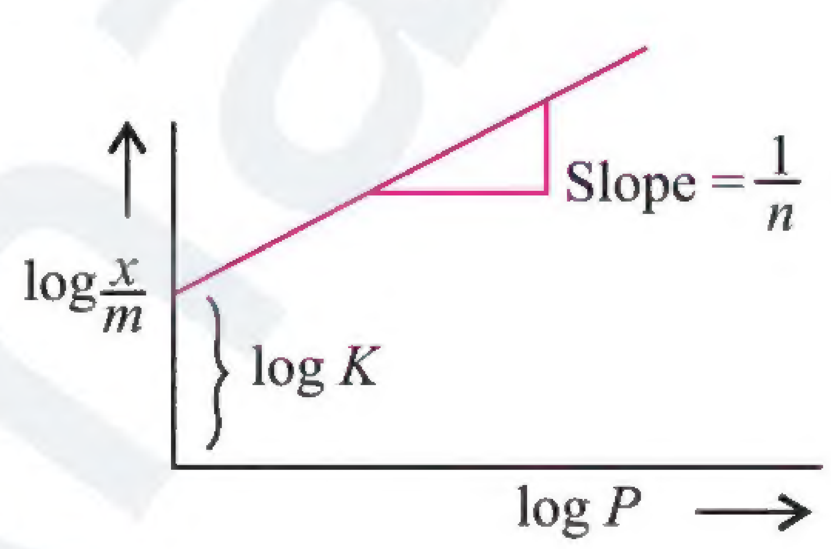
5 Surface Chemistry

OVERVIEW

1. *Adsorption* is a phenomenon of attracting and retaining the molecules of a substance at the surface of a solid or liquid rather than in bulk.
2. *Adsorbate* are the molecular species which concentrate at the surface.
3. The material on the surface of which adsorption takes place is called *adsorbent*.
4. If the concentration of adsorbate is more on the surface with respect to bulk, it is called *positive adsorption*. If it is less on the surface with respect to bulk it is called *negative adsorption*.
5. Greater the surface area of the adsorbent, greater is the adsorption.
6. Higher the critical temperature of a gas, greater is its adsorption.
7. Physical adsorption is due to van der Waals forces and is reversible. Chemisorption involves the formation of compounds on the surface and is irreversible.
8. At constant temperature, adsorption generally increases with pressure. Lower the temperature, greater is the effect of pressure.
9. Freundlich adsorption isotherm is

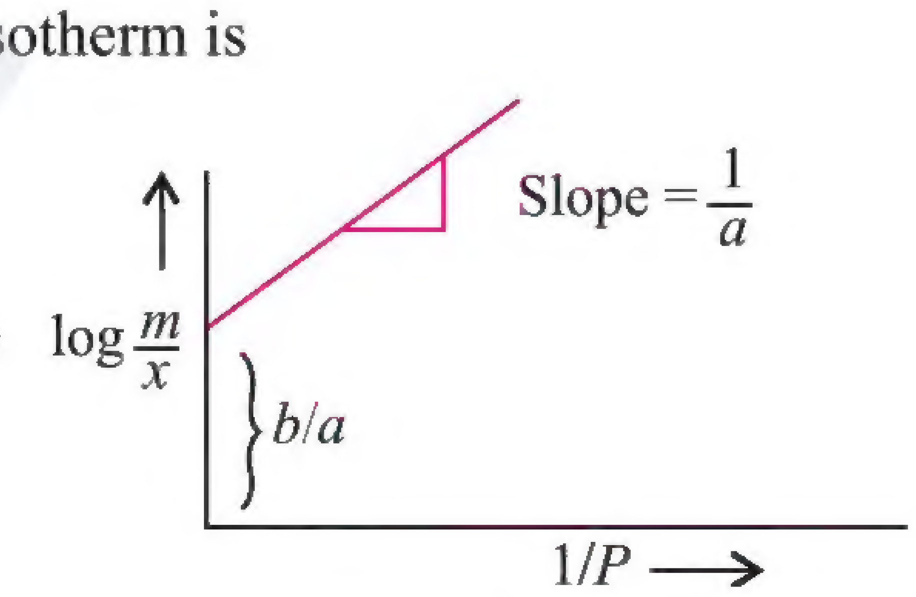
   $\frac{x}{m} = KP^{1/n}$ $(n > 1)$

   $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$

   i.e., plot of log x/m vs log P gives a straight line with slope = $1/n$ and intercept = log K.
10. Langmuir adsorption isotherm is

    $\frac{x}{m} = \frac{aP}{1+bP}$

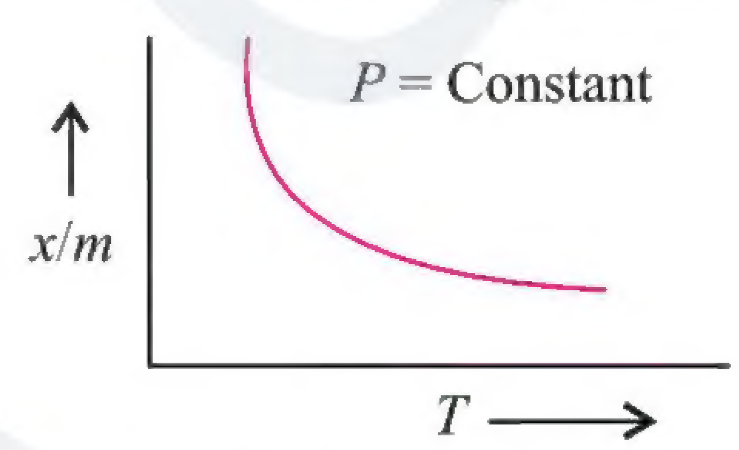
    

    where a and b are constants.

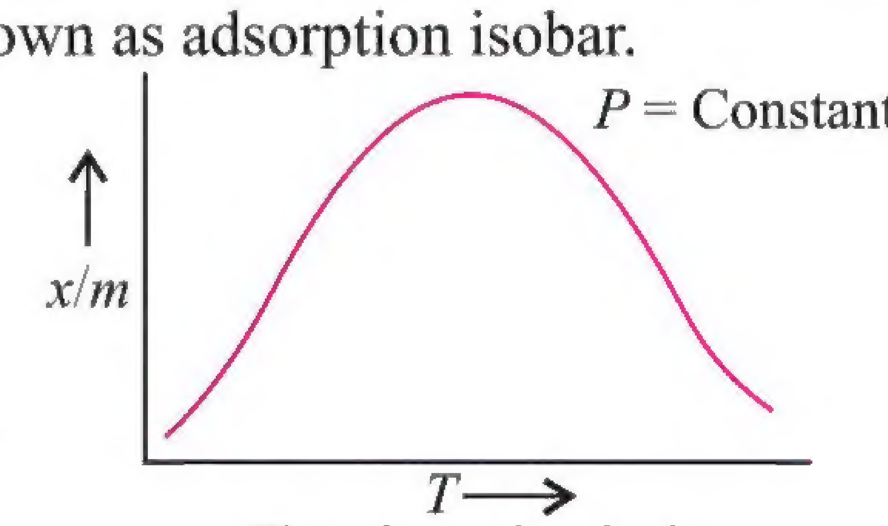
    or $\frac{m}{x} = \frac{b}{a} + \frac{1}{aP}$

    A plot of log m/x against $1/P$ gives a straight line with slope = $1/a$ and intercept = b/a.
11. Adsorption is generally temperature dependent. Most of the adsorption processes are exothermic and therefore adsorption decreases with increasing temperature.

    Adsorption isobars: A graph drawn between the degree of adsorption (x/m) and temperature (T) at a constant pressure of adsorbate gas is known as adsorption isobar.

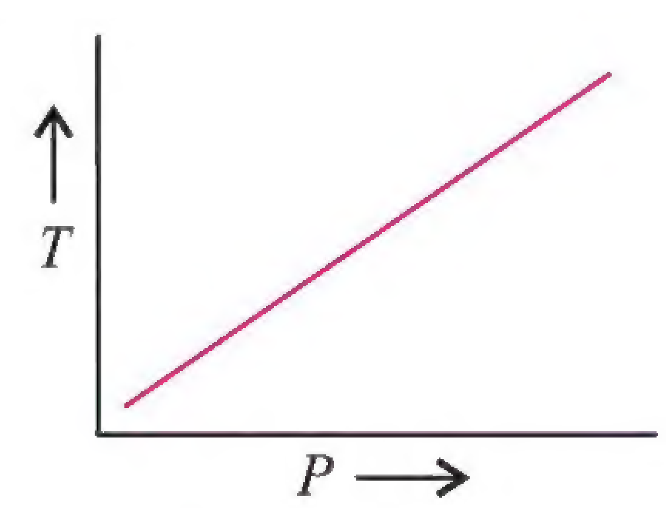
    

    Physisorption isobar

    Chemisorption isobar

    Adsorption isostere: The plot of temperature versus pressure for a given amount of adsorption is called adsorption isostere.

12. Colloids are classified in the following three different ways:
    - **a.** Based on the physical state of the dispersed phase and dispersion medium, there are 8 types (except gas in gas)
    - **b.** Based on the nature of interaction between dispersed phase and dispersion medium, i.e., as lyophilic and lyophobic colloids.
    - **c.** Based on the types of particles of the dispersed phase i.e., as multimolecular, macromolecular, and associated colloids.
13. Lyophilic sols are formed by organic substances such as starch, gum, proteins, etc. These are reversible. Lyophobic sols are formed by inorganic substances such as metals, their sulphides, etc. They are irreversible.

    Lyophilic sols are more stable than lyophobic due to their greater hydration in the solution.
14. Colloidal dispersions of sulphur, gold, etc., are multi-molecular. Those of polymers, e.g., starch, cellulose, proteins, nylon, rubber, etc., are *macromolecular* while a collodal sol of soap in water is *associated colloid.*

15. The aggregate of ions in an associated colloidal solution is called *ionic micelle*. The concentration above which these ionic micelles are formed is called *critical micellization concentration* (*CMC*) and the temperature above which they are formed is called *Kraft temperature* (T_K).

16. *Collodion* is a lyophilic colloidal sol of cellulose nitrate in ethyl alcohol.

17. Conversion of a freshly precipitated substance into colloidal sol by shaking with a suitable electrolyte is called *peptization*, e.g., $Fe(OH)_3$ ppt with $FeCl_3$ sol, AgI ppt with $AgNO_3$ or KI solution. The electrolyte should have a common ion.

18. According to Hardy Schulze rule, greater the valency of the oppositely charged ions of the electolyte, faster is the coagulation. The coagulating power of the ion is directly proportional to the fourth power of its valency. Thus, for a negatively charged sol, $Al^{3+} > Ba^{2+} > Na^{\oplus}$. For a positively charged sol, $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{\ominus}$

19. **Isoelectric point of colloids:** The $H^{\oplus}$ ions concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e., they are electrically neutral) is known as isoelectric point of colloid.

20. The conversion of a freshly precipitated substance into colloidal solution by shaking with a suitable electrolyte is called *peptization*.

21. The movement of colloidal particles under the influence of an electric field is called *electrophoresis*.

22. The process of changing the colloidal particles in a solution into an insoluble preciptate by the addition of some suitable electolytes is known as *coagulation*.

23. The minimum number of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal solution is called its *coagulation* or *flocculation value*.

24. The minimum number of milligrams of a lyophilic solution needed to protect 10 mL of gold solution by the addition of 1 mL of 10% NaCl is called gold number. Protective power is the reciprocal of gold number.

25. The colligative property used to determine the molecular masses of colloidal is called *osmotic pressure.*

26. The zig-zag movement of the colloidal particles in a colloidal sol is called *Brownian movement.*

27. The scattering of light by colloidal particles is called *Tyndall effect.*

28. A colloidal sol is a stable because all the colloidal particles in a colloidal sol carry the same charge.

29. A colloidal sol can be purified i.e., particles of the crystalloids can be separated from it by dialysis or ultrafiltration or ultra-centrifugation.

30. The separation of crystalloids from colloids by diffusion through parchment/animal membrane is called *dialysis*.

31. Ultra filters are prepared by treating filter paper with colloidion or gelation solution followed by hardening with formaldehyde.

32. In ultracentrifugation, the colloidal sol is taken in a tube rotated at high speed in ultracentrifuge. Colloidal particles settle down, which are separated and mixed with the dispersion medium.

33. Coagulation occurs (a) by addition of electrolyte, (b) by electrophoresis, (c) by mixing oppositely charged sols, (d) by prolonged dialysis, and (e) by heating or cooling.

34. Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of (a) oil-in-water type and (b) water-in-oil type.

35. The process of making emulsion is called *emulsification*.

36. To stabilize an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers.

37. The most common emulsifiers are soaps.

38. Milk is an emulsion of oil in water (fats in water) while cod liver oil is water in oil.

39. Presence of soluble soaps as emulsifying agent gives oil-in-water type emulsion while that of insoluble soaps results in water-in-oil type emulsion.

40. If on adding an electrolyte to an emulsion, conductance increases, it is oil-in-water type.

41. Latex is colloidal dispersion of rubber particles in water.

42. The swelling of gel when placed in water is called *imbibition.*

43. Some gels on shaking change into liquid which on standing again changes into gel. This property is called *thixotropy.*

44. A catalyst is a substance which can change the speed of a chemical reaction without being used up in the reaction. If it increases the speed of the reaction, it is called *positive catalyst* and *if* it decreases the speed of the reaction. It is called *negative catalyst.* Further, if the catalyst and the reactants are present in the same phase, it is called *homogeneous catalysis* but if they are in different phase, it is called *heterogeneous catalysis*. Homogeneous catalysis is explained by intermediate compound formation theory while heterogeneous catalysis is explained by *adsorption theory.*

45. Zeolites are aluminosilicates. They form an important class of *oxide* catalysts. On heating in vacuum they lose water of hydration and become porous. They are used as *shape-selective catalysts.*

46. Enzymes are biological catalysts. They are globular proteins some of which contain a non-protein component called *cofactor* for their activity. Their main characteristics are their *specificity*, *efficiency* (even in small amounts) and *activity at physiological temperature of 37°C* and *pH of 7.4.* Their action is explained by *lock and key model or by hand and glove model* (also called *induced-fit model*).

47. Enzyme-catalyzed reaction takes place in two steps as:
a. $E + S \rightleftharpoons ES$ (fast and reversible)
b. $ES \longrightarrow E + P$ (slow and rate determining)
(E is enzyme, S is substrate, and P is product)

48. **Auto catalysis:** In certain reactions, one of the products acts as a catalyst. In the initial stage, the reaction is slow but as soon as the product comes into existence, the reaction rate increases.

49. **Induced catalysis:** When one reaction influences the rate of another reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

50. Promoters are those substances which when added in small amount with the catalysts enhance the efficiency of catalyst.

51. Poisons are the substances which destroy the activity of the catalyst by their presence.

5.1 INTRODUCTION

Surface chemistry deals with the phenomenon that occurs at the surface or interfaces. There are several properties of substances, particularly of solids and liquids and solids and gases, which depend upon the nature of the surface or interface. An interface or surface is generally represented by separating the bulk phases by a dash or a slash. For example, the interface between a solid and a gas may be represented by solid–gas or solid/gas. The bulk phases that we consider in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particle of bulk phase. Many important phenomena, such as electrode processes, heterogeneous catalysis, corrosion, adsorption on solid or on solution surface, colloidal properties, etc., are important surface effects which are useful to understand many physical and chemical properties of the substances.

The subject of surface chemistry has many applications in industry, analytical work, and daily life situations. In this chapter, we will be studying some important features of surface chemistry such as adsorption, catalysis, and colloids including emulsions and gels.

5.2 ADSORPTION

Adsorption is essentially a surface phenomenon. There are several examples which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not penetrate deeper into the bulk. For example, when a small amount of finely divided charcoal is put into a vessel containing a gas, it is observed that the pressure of the gas first rapidly and then gradually decreases. The decrease in pressure of the gas is due to the accumulation of gas on the surface of charcoal. Figure 5.1 shows adsorption of a gas at the solid surface.

Fig. 5.1 Adsorption of a gas at the solid surface

The phenomenon of attracting and retaining the molecules of a substance on the surface rather than in the bulk of a solid or liquid resulting into higher concentration of the molecules on the surface is termed adsorption.

The molecular species or substance which concentrates or accumulates at the surface is termed *adsorbate* and the material on the surface of which adsorption takes place is called *adsorbent* (Fig. 5.2).

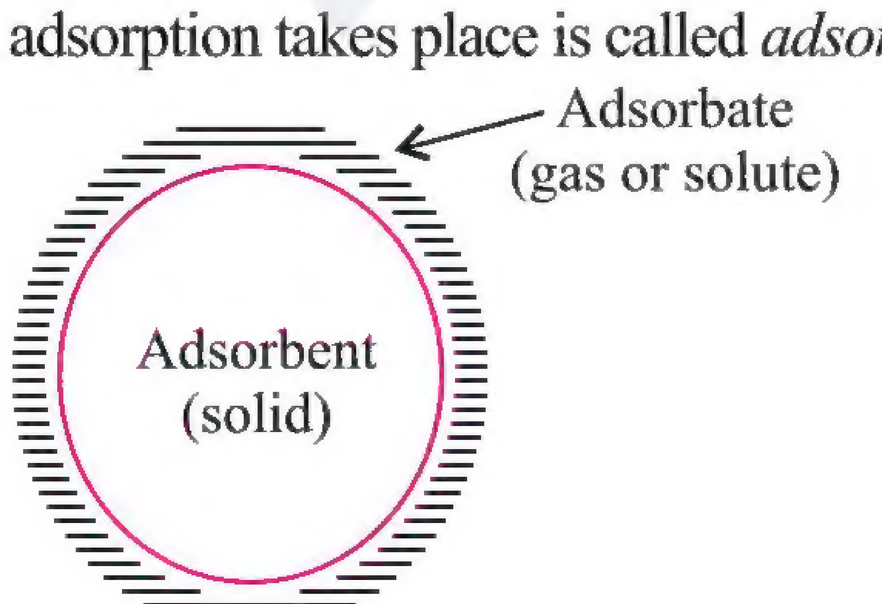


Fig. 5.2 Adsorbent and adsorbate

The adsorbent may be solid or a liquid and the adsorbate may be a gas or a solute in some solution.

The adsorption of gases on metal surfaces is called *occlusion*. A few examples of adsorption are as follows:

a. If a gas such as O_2, H_2, Cl_2, NH_3, or SO_2 is taken in a closed vessel containing powdered charcoal, its molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface. Solids, particularly in a finely divided state, have large surface area and therefore charcoal, silica gel, alumina gel, clay, colloids, and metals in finely divided state act as good adsorbents.

b. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

c. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

d. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surface can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called *desorption*.

5.2.1 Distinction Between Adsorption and Absorption

Adsorption is a phenomenon in which a substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent. On the other hand, absorption is a phenomenon in which the molecules of a substance are uniformally distributed throughout the bulk of the solid.

For example, when a chalk stick is dipped in ink the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes. Figure 5.3 illustrates adsorption, absorption, and sorption.

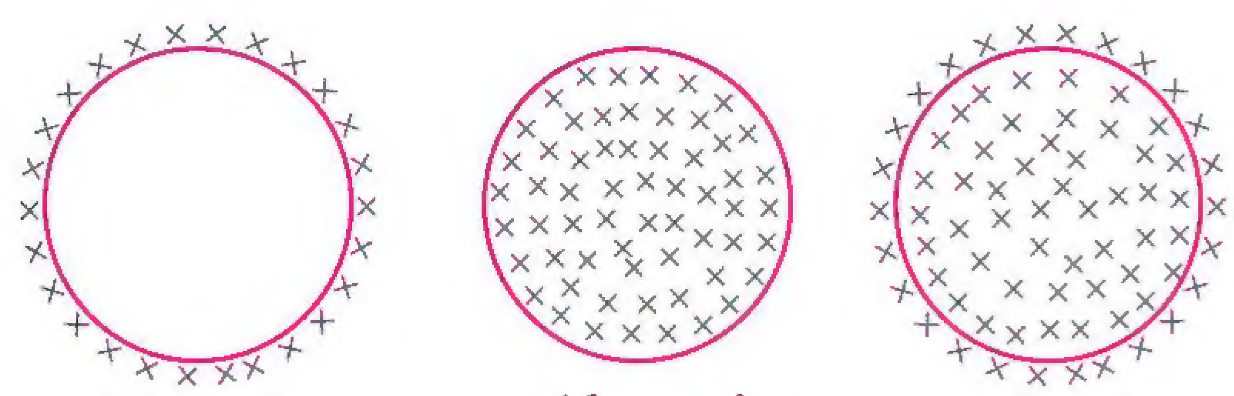


Fig. 5.3

The important points of difference between adsorption and absorption are listed in Table 5.1.

Table 5.1 Differences between adsorption and absorption

Adsorption	Absorption
a. It is a surface phenomenon i.e., it occurs only at the surface of the adsorbent.	**a.** It is a bulk phenomenon, i.e, it occurs throughout the body of the material.
b. In this phenomenon, the concentration on the surface of adsorbent is different from that in the bulk.	**b.** In this phenomenon, the concentration is same throughout the material.
c. Its rate is high in the beginning and then decreases till equilibrium is attained.	**c.** Its rate remains same throughout the process.

Positive adsorption: When the concentration of the adsorbate is more on the surface of adsorbent relative to its concentration in the bulk, it is called positive adsorption.

Negative adsorption: When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk, it is called negative adsorption. For example, in the case of some liquid solutions, it is observed that the concentration of the solute is less on the surface than in the bulk of the solution. This type of adsorption is called negative adsorption.

5.2.2 Mechanism of Adsorption

Adsorption arises because of the unbalanced forces on the surface of the adsorbent (Fig. 5.4). If we consider a solid, it is observed that a molecule present in the bulk of the solid is being uniformally attracted form all sides by the neighbouring molecules. As a result, there is no net pull on this molecule. However, a molecule which lies near the surface is being attracted only by molecules below it. Therefore, surface molecules experience a resultant downward attractive force within the solid. In other words, the surface is under strain or tension due to unbalanced forces. As a result, the surface of the solid tends to satisfy its residual forces by attracting and retaining the molecules of the adsorbate when brought in contact with them. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure. This shows that with the increase of surface area, the unbalanced attractive forces of the surface are also increased.

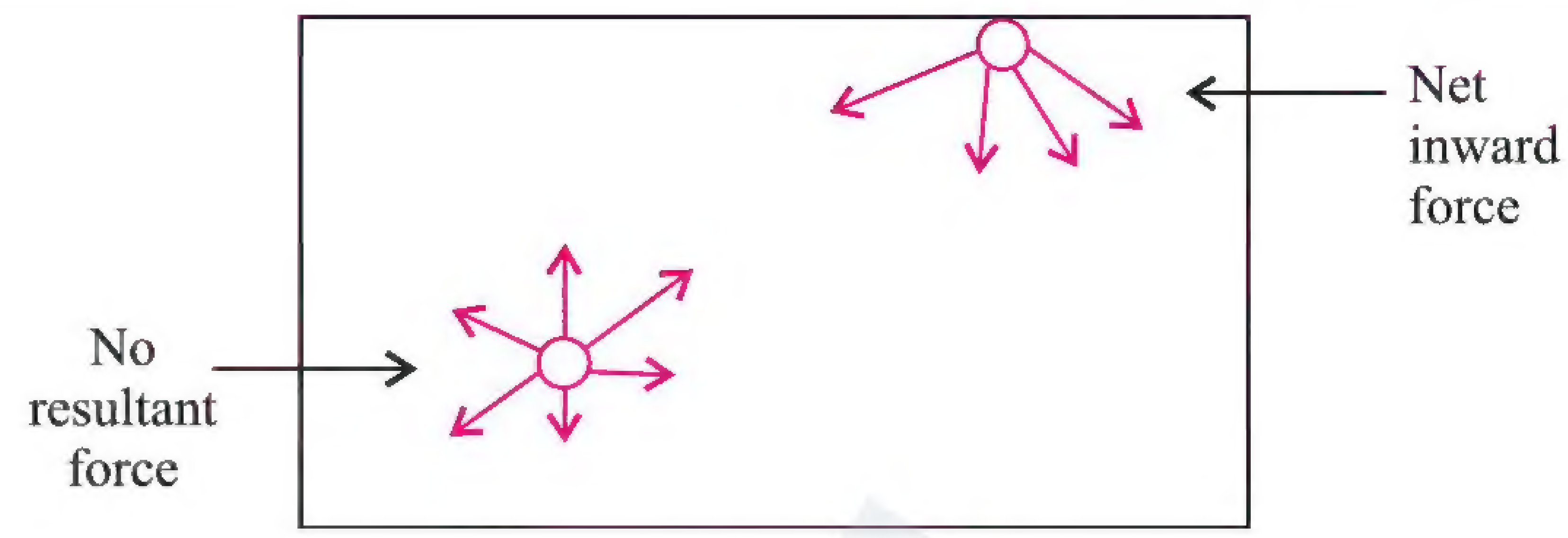


Fig. 5.4 Adsorption due to unbalanced forces on the surface of adsorbent

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in the residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to a decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by a decrease in the enthalpy as well as a decrease in the entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative, ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained and hence it is called *adsorption equilibrium*.

5.2.3 Types of Adsorption

Adsorption of gases on solid is mainly classified into two types, depending upon the nature of forces which hold the molecules of the adsorbate on the surface of the adsorbent.

a. Physical adsorption or physisorption

b. Chemical adsorption or chemisorption

a. Physical adsorption: If the particles of an adsorbate are held to the surface of the adsorbent by the physical forces such as van der Waals forces, the adsorption is termed as physical adsorption or physisorption. The attractive forces are weak, and therefore, these can be easily overcome either by increasing the temperature or by decreasing the pressure. In other words, physical adsorption can be easily reversed.

Following are the characteristics of physisorption:

i. Lack of specificity: A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals forces are universal.

ii. Nature of adsorbate: The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals forces are stronger near the critical temperatures. Thus, 1 g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630 K) than methane (critical

temperature 190 K) which is still more than 4.5 mL of dihydrogen (critical temperature 33 K).

iii. Reversible nature: Physical adsorption of a gas by a solid is generally reversible. Thus,

$$\text{Solid} + \text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

More of gas is adsorbed when pressure is increases as the volume of the gas decreases (Le-Chatelier's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle).

iv. Surface area of adsorbent: The extent of adsorption increases with an increase of the surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

v. Enthalpy of adsorption: No doubt, physical adsorption is an exothermic process, but its enthalpy of adsorption is quite low (20–40 kJ mol^{-1}). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals forces.

b. Chemical adsorption: When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical bonds, the adsorption is termed as chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. This type of adsorption is irreversible.

Following are the characteristics of chemisorption:

i. High specificity: Chemisorption is highly specific and will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

ii. Irreversibility: As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.

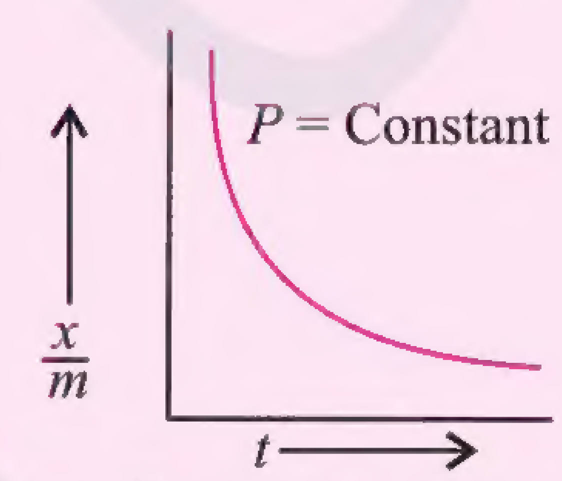
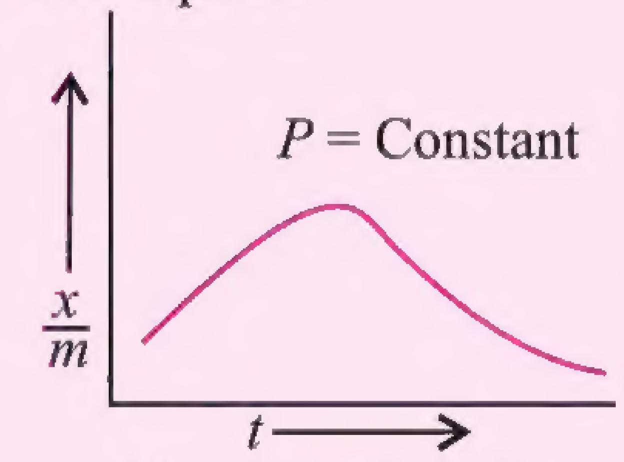
iii. Surface area: Like physical adsorption chemi-sorption also increases with increase of surface area of the adsorbent.

iv. Enthalpy of adsorption: The enthalpy of chemisorption is high (80–240 kJ mol^{-1}) as it involves chemical bond formation.

Difference between physical adsorption and chemical adsorption

The main differences between physical adsorption and chemical adsorption are summed up in Table 5.2.

Table 5.2 Difference between physisorption and chemisorption

Physisorption	Chemisorption
a. The forces operating in these cases are weak van der Waals forces.	**a.** The forces operating in these cases are similar to those of a chemical bond.
b. The heat of adsorption is low, viz., about 20–40 kJ mol^{-1}.	**b.** The heat of adsorption is high, viz., about 80–240 kJ mol^{-1}.
c. No compound formation takes place in these cases	**c.** Surface compounds are formed.
d. The process is reversible, i.e., desorption of the gas occurs by increasing the temperature or decreasing the pressure.	**d.** The process is irreversible. Efforts to free the adsorbed gas give some definite compound.
e. This type of adsorption decreases with increase of temperature.  Physisorption isobar	**e.** This type of adsorption first increases with increase of temperature and then decreases. The effect is called activated adsorption.  Chemisorption isobar
f. It is not specific in nature i.e., all gases are adsorbed on all solids to some extent.	**f.** It is specific in nature and occurs only when there is some possibility of compound formation between the gas being adsorbed and the solid adsorbent.
g. The amount of the gas adsorbed is related to the ease of liquefication of the gas.	**g.** There is no such correlation.
h. It forms multimolecular layer.	**h.** It forms unimolecular layer.
i. The rate of adsorption increases with increase in pressure of adsorbate.	**i.** The rate of adsorption usually decreases as the pressure increases.

5.2.4 Factors Affecting Adsorption of Gases on Solids

The extent of adsorption of a gas on a solid surface is affected by the following factors:

- **a.** Nature of gas
- **b.** Nature and specific area of adsorbent
- **c.** Effect of pressure
- **d.** Effect of temperature
- **e.** Activation of absorbent

Nature of the Gas

Different gases are adsorbed to different extents by the same adsorbent at same temperature. The physical adsorption is non-specific in nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, under given conditions of temperature and pressure, the easily liquefable gases such as CO_2, HCl, and NH_3 are adsorbed more than the permanent gases such as H_2, N_2, or O_2. This is illustrated in Table 5.3 in which the volumes of different gases (reduced to NTP conditions) adsorbed by 1 g of charcoal at 288 K have been given. The critical temperatures of the gases are also included in Table 5.3.

Table 5.3 Volume of gases at NTP adsorbed by 1 g of charcoal at 288 K

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (cc)	4.7	8.0	9.3	16.2	48	72	181	3 8 0
Critical temperature (K)	33	126	134	190	304	324	406	4 3 0

From the table, it may be seen that higher the critical temperature of a gas, greater is the amount of that gas adsorbed. In other words, a gas which is more easily liquefiable or is more soluble in water is more readily adsorbed. This relationship is not surprising as the critical temperature of a gas is related to the intermolecular forces which is an important factor for adsorption too.

Nature and Specific Area of Adsorbent

The extent of adsorption of a gas depends upon the nature of adsorbent. Most common adsorbents are activated charcoal, finely divided metals, and metal oxides (silica gel, aluminium oxide, etc.). Each of these have their own adsorption properties. The larger the surface area of the solid, the greater would be its absorbing capacity. Therefore, the porous and finely divided forms of adsorbents absorb large quantities of adsorbate.

Effect of Pressure

The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm. The extent of adsorption is usually expressed as x/m where x is the mass of adsorbate and m is the mass of the adsorbent. The adsorption isotherm is shown in Fig. 5.5.

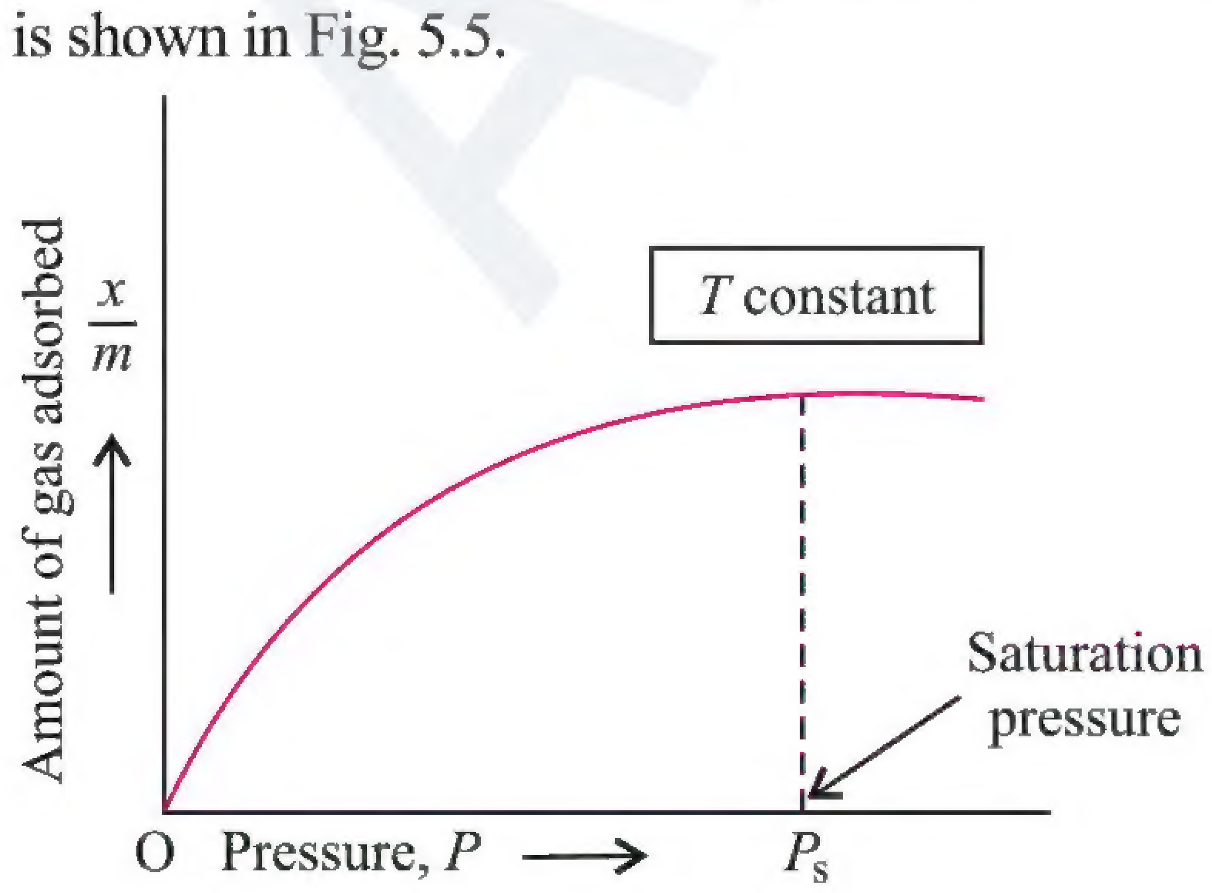


Fig. 5.5 Adsorption isotherm

It is clear from the figure that the extent of adsorption (x/m) increases with pressure and reaches maximum, corresponding to pressure P_s, called *equilibrium pressure*. Since adsorption is a reversible process, desorption also takes place simultaneously. At this pressure (P_s), the amount of gas adsorbed becomes equal to the amount of gas desorbed so that the extent of adsorption becomes constant even though the pressure is increased. This state is also called saturation state and P_s is called saturation pressure.

Adsorption isotherm: Scientists have explained adsorption in terms of some empirical mathematical relations called adsorption isotherm. The most common types are:

a. Freundlich adsorption isotherm: In 1909, Freundlich gave a mathematical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed as:

$$\frac{x}{m} = KP^{1/n} \ (n > 1) \quad ...(i)$$

where x is the mass of gas adsorbed on mass m of the adsorbent at pressure P; K and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in form of a curve where the mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.6). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with an increase in temperature. These curves always seem to approach saturation at high pressure.

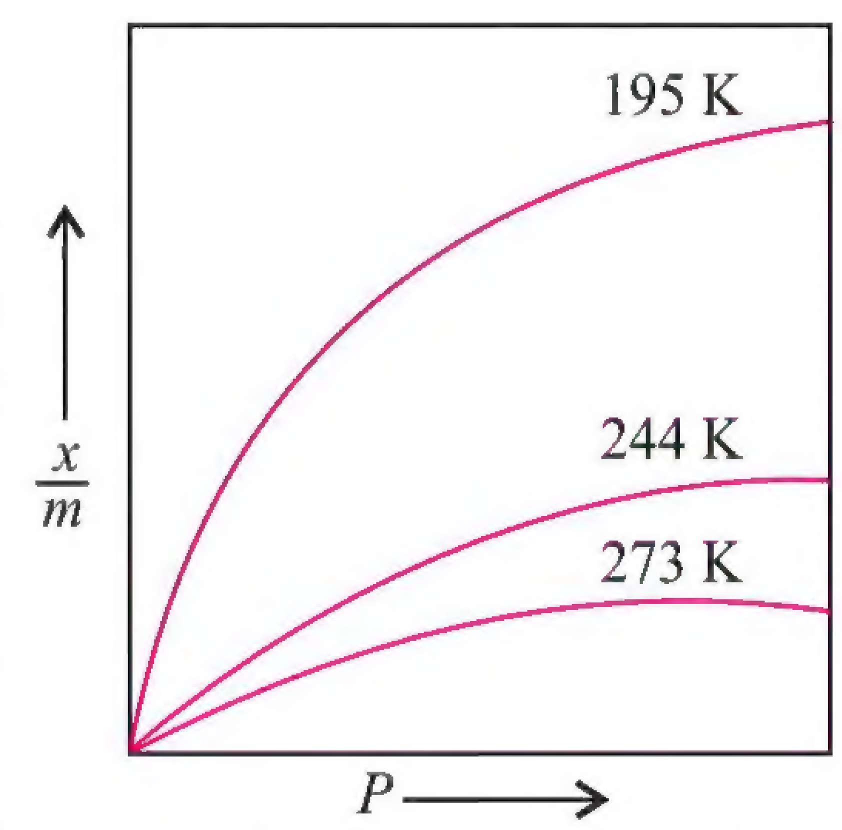


Fig. 5.6 Adsorption isotherm

Calculation of K and n of adsorption isotherm

Taking logarithm of Eq. (i),

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P \quad ..(ii)$$

The validity of Freundlich isotherm can be verified by plotting log (x/m) on y-axis (ordinate) and log P on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.7). The slope of the straight line gives the value of $1/n$. The intercept on the y-axis gives the value of log K.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $1/n$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, Eq. (ii) holds good over a limited range of pressure.

From the Freundlich isotherm, the following observation can be easily observed (Fig. 5.7):

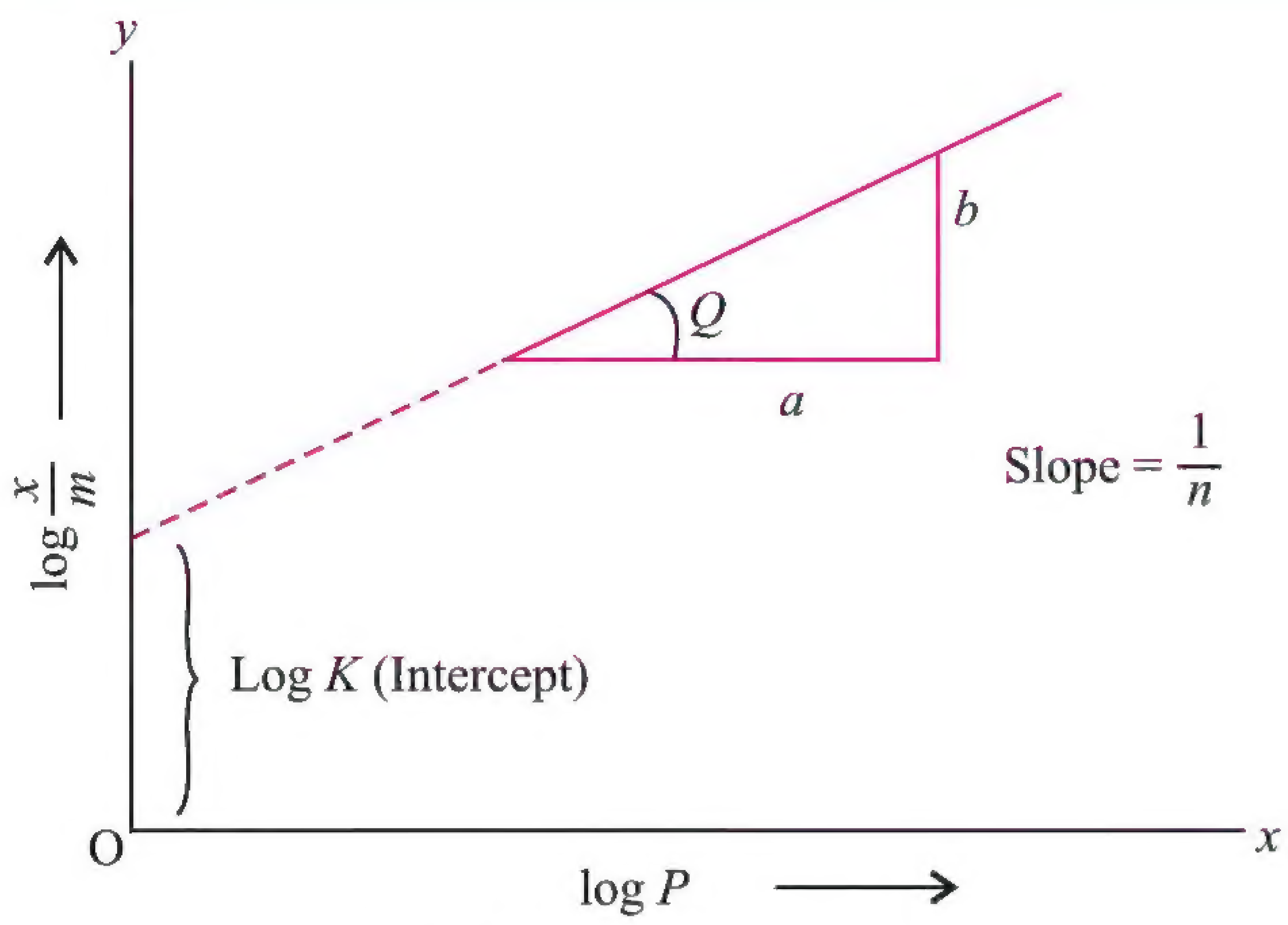


Fig. 5.7 Freundlich isotherm

i. **At low pressure:** When $\frac{1}{n} = 1$, $\frac{x}{m} = KP$, i.e., $x/m \propto P$ which means that x/m is directly proportional to the pressure. The graph is almost straight line. It follows first-order kinetics.

ii. **At high pressure:** When $\frac{1}{n} = 0$, $\frac{x}{m}$ = constant, which means that adsorption is independent of pressure. The graph becomes almost constant. This can be expanded as:

$$\frac{x}{m} = KP^{1/n}$$

$$\Rightarrow \quad \frac{x}{m} = KP^0 \qquad \left(\frac{1}{n} = 0\right)$$

$$= K \qquad (P^0 = 1)$$

It follows zero-order kinetics.

iii. **At intermediate range of pressure:** At intermediate range of pressure x/m will depend upon the power of pressure which lies between 0 and 1. This can be expressed as:

$$\frac{x}{m} = KP^{1/n}$$

where n can take any whole number.

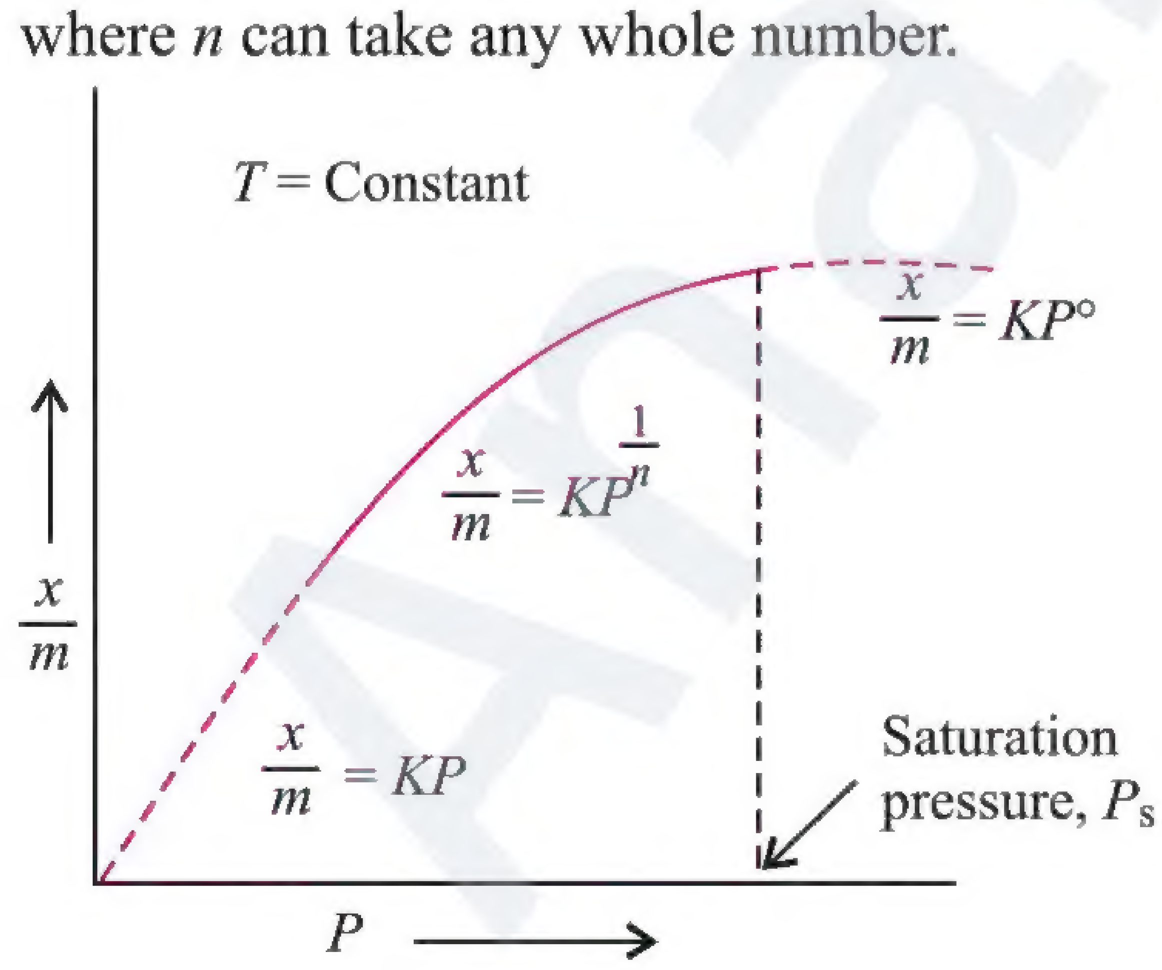


Fig. 5.8 Variation of x/m with increase in pressure at constant temperature (general adsorption isotherm)

b. **Langmuir adsorption isotherm:** One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases. This is named as the Langmuir adsorption isotherm. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of following two opposing processes:

i. Adsorption of gas molecules on the surface of the solid.

ii. Desorption of adsorbed molecules form the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas was only one molecule thick, i.e., unimoleuclar. Since such type of adsorption is obtained in the case of chemisorption, Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation:

$$\frac{x}{m} = \frac{aP}{1+bP} \qquad \text{...(i)}$$

where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{P} \text{ (at very high pressure)} \qquad \text{...(ii)}$$

At very low pressure, Eq. (i) is reduced to

$x/m = aP$ (at very low pressure) ...(iii)

In order to determine the parameters a and b, Eq. (i) may be written in its inverse form:

$$\frac{m}{x} = \frac{1+bP}{aP} = \frac{b}{a} + \frac{1}{aP} \qquad \text{...(iv)}$$

A plot of m/x against $1/P$ gives a straight line with slope and intercept equal to $1/a$ and b/a, respectively. Thus, both parameters can be determined.

The Langmuir isotherm, in the form of Eq. (i) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer or a unimolecular adsorbed layer is formed. A plot of x/m versus P is shown in Fig. 5.9.

At low pressures, according to Eq. (iii), x/m increases linearly with P. At high pressure, according to Eq. (ii), x/m becomes constant, i.e., the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 5.9.

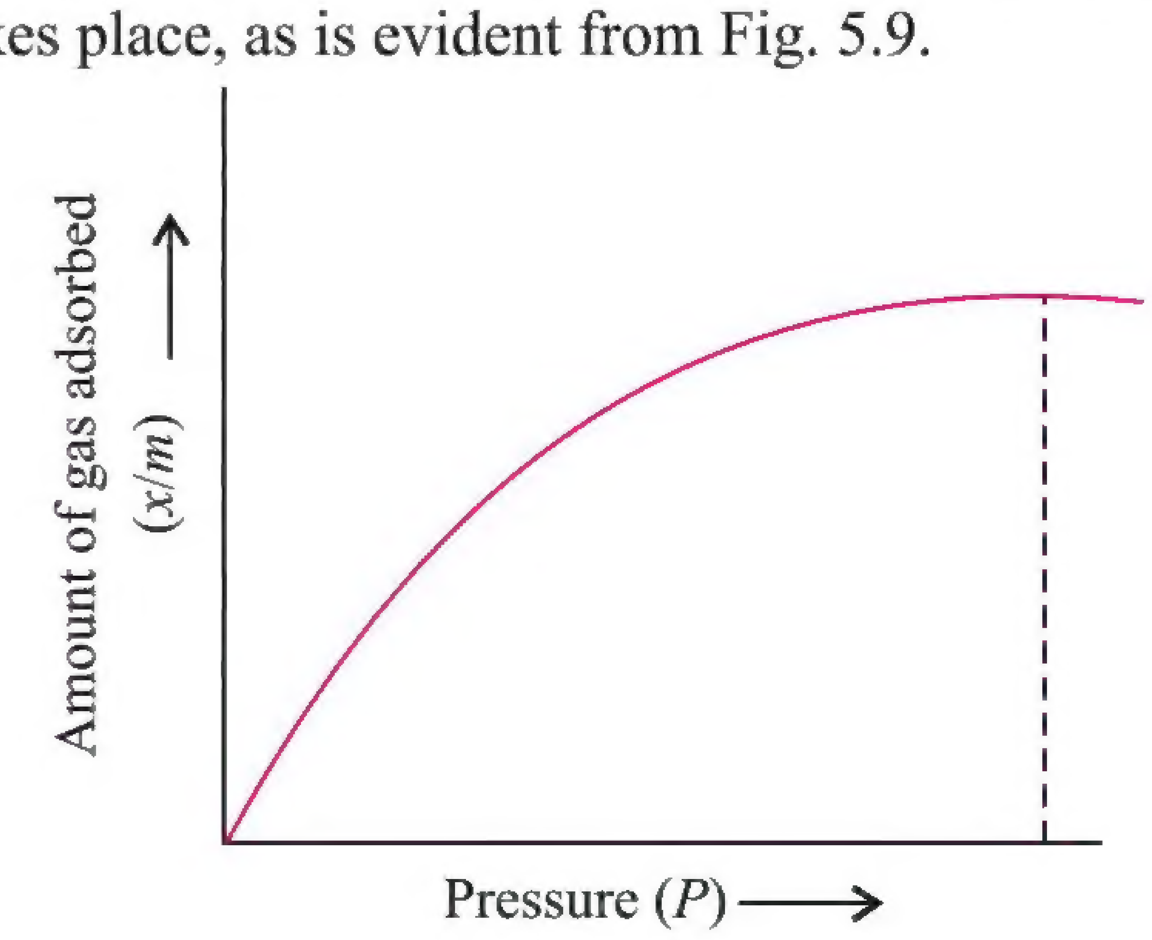


Fig. 5.9

Effect of Temperature

Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic, therefore, the reverse process, i.e., desorption, is endothermic. If the above equilibrium is subjected to change in temperature, then according to Le-Chatelier's principle, with decrease in temperature adsorption will increase and vice-versa. Thus, with the increase in temperature at constant pressure, the extent of adsorption (x/m) will decrease. However, this is true only for physical adsorption as shown in Fig. 5.10(a). In case of chemisorption, the adsorption initially increases with rise in temperature and then decreases as shown in Fig. 5.10(b).

This behaviour is expected because, like all chemical reactions, some activation energy is required for chemisorption. At low temperature, x/m is small. As temperature is increased, the molecules of the adsorbate gain energy and become equal to activation energy so that proper bonds are formed with the adsorbent molecules. Therefore, initially, the amount of gas adsorbed increases with rise in temperature. Further increase of temperature will increase the energy of molecules which have already been adsorbed. This would increase the rate of desorption and, therefore, decrease the extent of adsorption.

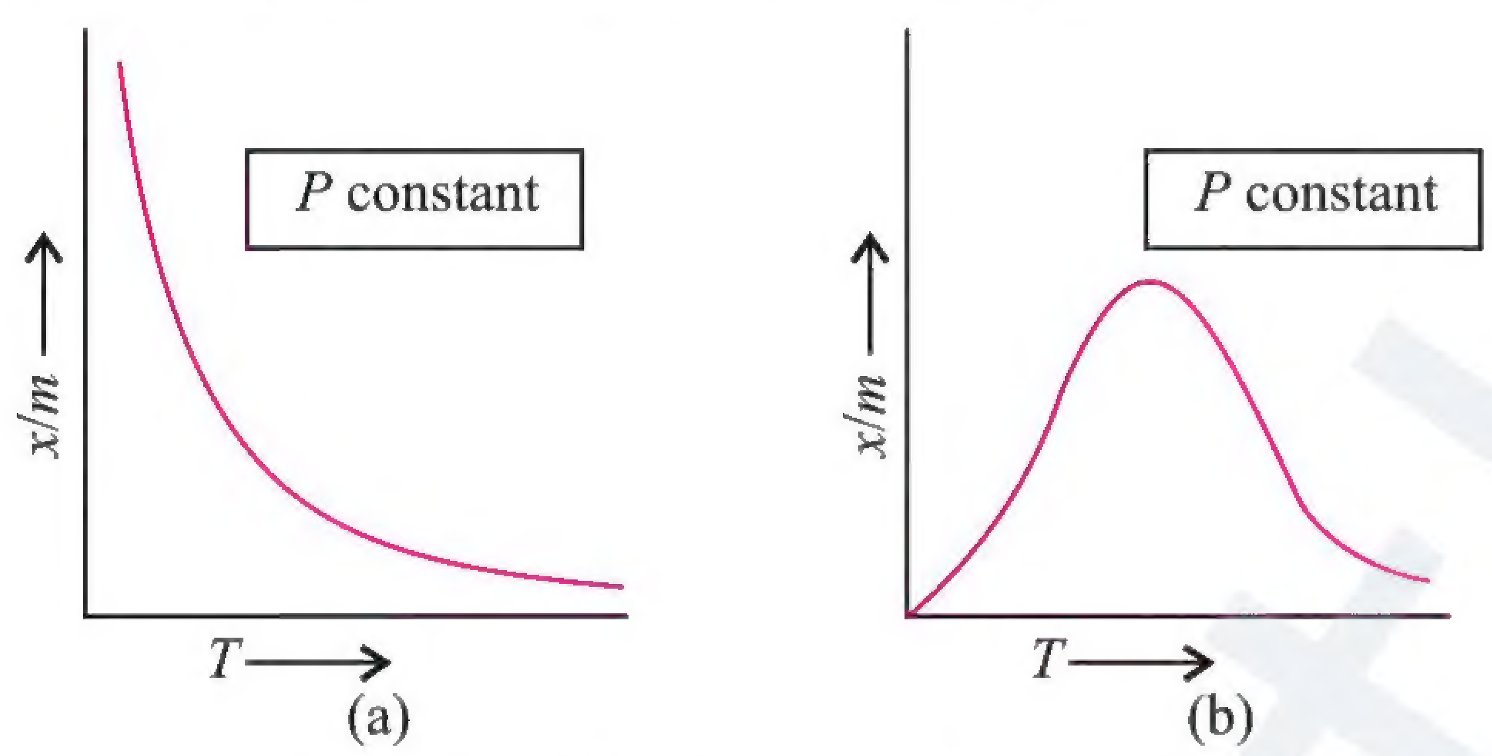


Fig. 5.10 Adsorption isobars for (a) physical adsorption and (b) chemical adsorption

The graph between the extent of adsorption and temp-erature at constant pressure is called *adsorption isobar*.

Activation of the Solid Adsorbent

Activation of the solid adsorbent means increasing the adsorbing power of an adsorbent. This is usually done by increasing the surface area (or the specific area) of the adsorbent which can be achieved in any of the following ways:

a. By making the surface of the adsorbent rough, e.g., by mechanical rubbing or by chemical action or by depositing finely dispersed metals on the surface of the adsorbent by electroplating.

b. By subdividing the adsorbent into smaller pieces or grains. No doubt this method increases the surface area but it has a practical limitation, that is, if the adsorbent is broken into very fine particles that it becomes almost powder, then the penetration of the gas becomes difficult and this obstructs adsorption.

c. By removing the gases already adsorbed, e.g., charcoal is activated by heating in superheated steam or in vacuum at a temperature between 623 and 1273 K.

5.2.5 Adsorption from Solution Phase

The process of adsorption can take place from solutions also. It is observed that solid adsorbents adsorb certain solutes from solution in preference to other solutes and solvents. For example, animal charcoal decolourizes impure sugar by adsorbing colouring dye in preference to sugar molecules.

Similarly, the litmus solution when shaken with charocal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of Magneson reagent. The colour is due to adsorption of magneson. The following observation have been made in the case of adsorption from solution phase:

a. The extent of adsorption decreases with an increase in temperature.

b. The extent of adsorption increases with an increase of surface area of the adsorbent.

c. The extent of adsorption depends on the concentration of the solute in solution.

d. The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

Freundlich adsorption and Langmuir adsorption isotherms have been found to be applicable in the adsorptions from solutions. Temperature dependence here also is similar to that for the adsorption of gases. However, in place of equilibrium pressure, we use equilibrium concentrations of the adsorbates in the solution and the isotherms take the form

$$\frac{x}{m} = Kc^{1/n} \qquad \text{...(i)}$$

Taking logarithms, Eq. (i) becomes

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log c$$

A graph between x/m and c has been found to be similar to one shown for x/m and P for gases on solid (Fig. 5.8).

From the graph, the values of $1/n$ and $\log K$ can be calculated as slope and intercept, respectively.

Similarly, Langmuir adsorption isotherm may be written as:

$$\frac{x}{m} = \frac{ac}{1 + bc}$$

The parameters of above equations can be determined by the method described earlier for adsorption of gases on solids.

5.2.6 Application of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed below:

a. Production of high vacuum: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

b. In curing disease: A number of drugs are used to kill germs by getting adsorbed on them.

c. Froth floatation process: A low-grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.

d. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes such as eosin, fluorescein, etc., and thereby producing a characteristic colour at the end point.

e. **Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

f. **In ion-exchange resin:** The organic polymers containing groups such as –COOH, $–SO_3H$, and – NH_2, etc., possess the property of selective adsorption of ions from solutions. These are quite useful in the softening of water.

g. **Surfactants:** Surfactants work as emulsifiers in the manufacture of emulsion. Emulsifiers work on the principle of adsorption.

h. **Gas masks:** Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

i. **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

j. **Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities.

k. **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. The manufacture of ammonia using iron as a catalyst, the manufacture of H_2SO_4 by contact process, and the use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

l. **Separation of inert gases:** Due to the difference in the degree of adsorption of gases by charcoal, mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

ILLUSTRATION 5.1

What is physical adsorption?

Sol. If the adsorbate is held on a surface by weak van der Waals forces, the adsorption is called physical adsorption.

ILLUSTRATION 5.2

What is sorption?

Sol. Sorption is the process in which adsorption and absorption take place simultaneously, e.g., dyeing of cotton fibres by azo dyes.

ILLUSTRATION 5.3

Why are powdered substances more effective adsorbent than their crystalline forms?

Sol. Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

ILLUSTRATION 5.4

How do size of particles of adsorbent, pressure of gas, and prevailing temperature influence the extent of adsorption of a gas on a solid?

Sol.

a. Smaller the size of the particles of an adsorbent, greater is the surface area and greater is the adsorption.

b. At constant temperature, adsorption first increases with increase of pressure and then attains equilibrium at high pressures.

c. In physical adsorption, it decreases with increase of temperature but in chemisorption, first it increases and then decreases.

ILLUSTRATION 5.5

Why physisorption is multi-molecular whereas chemisorption is unimolecular?

Sol. Chemisorption takes place as a result of the reaction between adsorbent and adsorbate. When the surface of the adsorbent is covered with one layer, no further reaction can take place. Physisorption is simply by van der Waals forces. So any number of layers may be formed one over the other on the surface of the adsorbent.

ILLUSTRATION 5.6

Compare the heat of adsorption for physical and chemical adsorption?

Sol. The heat of adsorption for chemical adsorption is high (of the order of 80–400 kJ mol^{-1}) while the heat of adsorption for physical adsorption is low (of the order of 20–40 kJ mol^{-1}).

ILLUSTRATION 5.7

In the case of chemisorption, why adsorption first increases and then decreases with temperature?

Sol. Chemisorption involves activation energy. The initial increase in chemisorption is due to the fact that the heat supplied acts as activation energy and more and more molecules of adsorbate gain energy and possess energy greater than activation energy. Therefore, adsorption increases with increase in temperature. Further increase will increase the energy of the molecules absorbed and will also increase the rate of desorption. Therefore, the extent of adsorption decreases.

ILLUSTRATION 5.8

Which will be adsorbed more readily on the surface of charcoal and why—NH_3 or CO_2?

Sol. NH_3 has higher critical temperature than CO_2, i.e., NH_3 is more liquefiable than CO_2. Hence, NH_3 has greater intermolecular forces of attraction and hence will be adsorbed more readily.

ILLUSTRATION 5.9

Give the expression of Freundlich isotherms.

Sol. $\frac{x}{m} = KP^{1/n}$ or $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$

where m is the mass of the adsorbent and x that of adsorbate, P is the pressure of the gas, and n is an integer.

ILLUSTRATION 5.10

What is meant by chemical adsorption?

Sol. If the adsorbate is held on the surface of the adsorbent as a result of chemical reaction forming surface compounds, it is called chemical adsorption.

ILLUSTRATION 5.11

What is desorption?

Sol. The process of removal of adsorbed substance is called desorption.

ILLUSTRATION 5.12

What is occlusion?

Sol. The adsorption of gases on the surface of metals is called occlusion.

ILLUSTRATION 5.13

Explain the following observations.

a. Sun looks red at the time of sunset.

b. Rate of physical adsorption decreases with rise in temperature.

c. Physical adsorption is multilayered while chemical adsorption is monolayered.

Sol.

a. At the time of sunset, the sun is at horizon. The light emitted by the sun has to travel a relatively longer distance through the atmosphere. As a result, blue part of light is scattered away by the particulate in the atmosphere causing red part to be visible.

b. Gas (adsorbate) + Solid (adsorbent)

$$\underset{\text{Evaporation}}{\overset{\text{Condensation}}{\rightleftharpoons}} \text{Gas adsorbed on solid + Heat}$$

Physical adsorption is an exothermic process. At equilibrium as the temperature is increased, by Le-Chaterlier's principle, the equilibrium shifts in the backward direction, i.e., adsorption decreases.

c. Physical adsorption involves van der Waals forces, so any number of layers may be formed one over the other on the surface of the adsorbent. Chemical adsorption takes place as a result of the reaction between adsorbent and adsorbate. When the surface of adsorbent is covered with one layer, no further reaction can take place.

ILLUSTRATION 5.14

How is adsorption of a gas related to its critical temperature?

Sol. Higher the critical temperature of a gas, greater the ease of liquefication, i.e., greater the van der Waals forces of attraction and hence greater the adsorption.

ILLUSTRATION 5.15

List four applications of adsorption.

Sol.

a. Heterogeneous catalysis is based on the adsorption of gases on solid.

b. Chromatograph is based on differential adsorption.

c. Charge on colloidal solution is due to selective adsorption of common ions on the surface.

d. Carbon particles from smoke get adsorbed on the surface of electrodes of cotterell smoke precipitators.

ILLUSTRATION 5.16

In an experiment, 200 mL of 0.5 M oxalic acid is shaken with 10 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 M. The amount of adsorption (x/m) is

a. 0.9 **b.** 1.8 **c.** 0.180 **d.** 0.09

Sol.

c. Mass of oxalic acid adsorbed by 10 g charcoal

$= 200 \times 10^{-3} (0.5 - 0.4) \times 90 = 1.8$ g

(Mw or oxalic acid = 90 g mol^{-1})

The amount of adsorption

$$\frac{x}{m} = \frac{1.8}{10} = 0.18$$

ILLUSTRATION 5.17

2.0 g of charcoal is placed in 100 mL of 0.05 M CH_3COOH to form an adsorbed mono-acidic layer of acetic acid molecules and thereby the molarity of CH_3COOH reduces to 0.49. The surface area of charcoal is 3×10^2 m^2 g^{-1}. The surface area of charcoal adsorbed by each molecule of acetic acid is

a. 1.0×10^{-18} m^2 **b.** 1.0×10^{-19} m^2

c. 1.0×10^{13} m^2 **d.** 1.0×10^{-22} m

Sol.

a. CH_3COOH adsorbed = 0.5 – 0.49 = 0.01 M

Number of molecules adsorbed $= 0.01 \times \frac{100}{1000} \times 6 \times 10^{23} = 6 \times 10^{20}$

Total area of charcoal $= 2 \times 3 \times 10^2 = 600$ m^2

$\Rightarrow$ Area per molecule $= \frac{600}{6 \times 10^{20}} = 1 \times 10^{-18}$ m^2

ILLUSTRATION 5.18

Which of the following statements is not true?

a. Both physisorption and chemisorption are exothermic.

b. Physisorption takes place with decrease of free energy whereas chemisorption occurs with increase of free energy.

c. Physisorption requires low activation energy but chemisorption requires high activation energy.

d. The magnitude of chemisorption increases and that of physisorption decreases with rise in temperature.

Sol.

b. For physisorption and chemisorption free energy change (ΔG) is negative.

ILLUSTRATION 5.19

The rate of chemisorption

a. increases with decrease in temperature
b. increases with increase in temperature
c. increases with decrease in the pressure of gas
b. is independent of the pressure of gas

Sol.

b. Chemisorption involves high activation energy and increases to a maximum value with rise in temperature.

ILLUSTRATION 5.20

Which of the two, He and Ne, gets adsorbed on the surface of charcoal more readily and why?

Sol. Ne will get adsorbed to more extent because it has large surface area, therefore, more van der Waals forces of attraction. Also it is more easily liquifiable as compared to He. More easily liquefiable gases are adsorbed to a greater extent.

ILLUSTRATION 5.21

Adsorption, if spontaneous, is exothermic. Explain.

Sol. Adsorption is accompanied by decrease in entropy, i.e., ΔS = –ve. If it is spontaneous than ΔG should be negative

$\Delta G = \Delta H - T\Delta S$.

Since ΔS is –ve (entropy decreases in the process of adsorption), ΔG will be negative, only if ΔH = –ve, i.e., if the process is exothermic.

CONCEPT APPLICATION EXERCISE 5.1

1. Explain the following terms
   a. Adsorption b. Adsorbate c. Adsorbent
2. Discuss the effect of pressure and temperature on the adsorption of gases by solids.
3. How is the adsorption of a gas related to its critical temperature?
4. Derive the following:
   a. Langmuir isotherm b. Freundlich isotherm
5. Write differences between physisorption and chemisorption.
6. Which of the two, adsorption or absorption, is surface phenomenon?
7. Why finely divided substance is more effective as an adsorbent?
8. Discuss different types of adsorption and their properties.

5.3 CATALYSIS

The substances which alter the velocity of a reaction and themselves remain chemically and quantitatively unchanged after the reaction; are known as *catalysts*, and the phenomenon is known as *catalysis*.

Catalysts are not consumed in the reaction, hence very small non-stoichiometric quantities are generally required. For example, when potassium chlorate heated strongly decomposes slowly giving dioxygen, the decomposition occurs in the temperature range of 653–873 K.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473–633 K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. Thus, manganese dioxide acts as a catalyst for the above reaction.

5.3.1 PROMOTERS AND POISONS

Promoters are substances that, if present along with a catalyst, enhances the activity of a catalyst. For example, in Haber's process, for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Mo(s)}]{\text{Fe(s)}} 2NH_3(g)$$

Poisons are substances that decrease the activity of a catalyst. These substances are called catalytic poisons. For example:

a. The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.
b. The presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

5.3.2 TYPES OF CATALYSIS

Based on the type of catalytic reactions, catalysis is of following types:

a. Positive catalysis: If a catalyst increases (accelerates) the rate of a reaction, it is called a positive catalyst and the phenomenon is called positive catalysis.

Positive catalyst increases the rate by lowering the activation energy of reaction. A catalyst provides an entirely new path for the reaction in which a newly activated intermediate complex of lower potential energy is formed.

This means that the catalyst provides a new pathway of lower activation energy. Consequently, the fraction of the total number of collisions possessing lower activation energy is increased and hence the rate of reaction also increases. Figure 5.11 gives an energy diagram which depicts the effect of a catalyst on the activation energy. The solid line shows the path for uncatalyzed reaction and the dotted line shows the path adopted by catalyzed reaction.

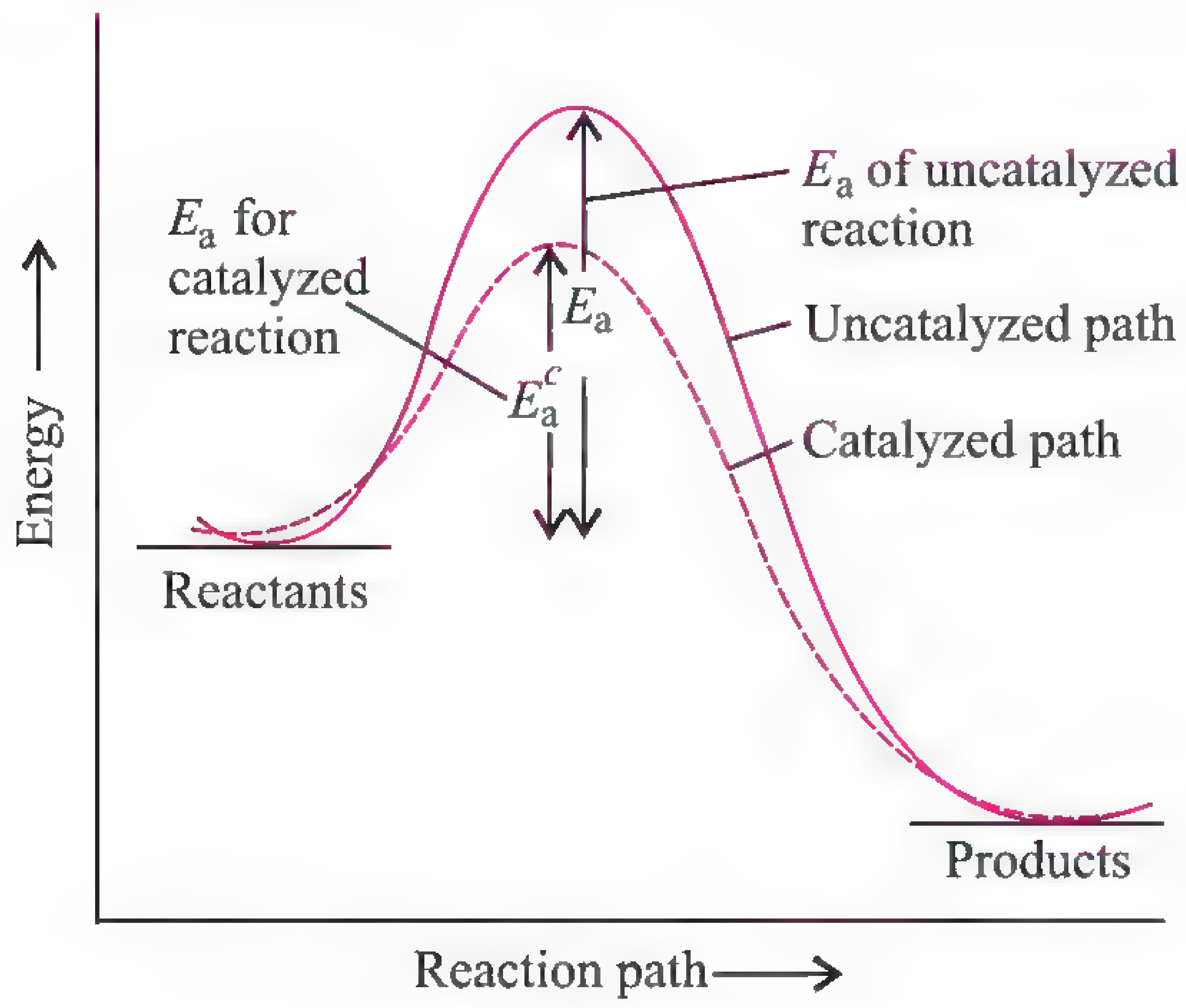


Fig. 5.11 Comparison of activation energies of a catalyzed and an uncatalyzed reaction

Some examples of positive catalysis are as follows:

i. Decomposition of H_2O_2 in the presence of colloidal platinum

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

ii. Hydrogenation of vegetable oil in the presence of nickel

$$\text{Vegetable oil(l)} + H_2(g) \xrightarrow{Ni(s)} \text{Ghee(s)}$$

iii. Formation of methane in the presence of nickel

$$CO(g) + 3H_2(g) \xrightarrow{Ni(s)} CH_4(g) + H_2O(g)$$

iv. Oxidation of sulphur dioxide in the presence of nitric oxide

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

b. Negative catalysis: If a catalyst decreases (retards) the rate of a reaction, it is called negative catalyst and the phenomenon is called negative catalysis. For example:

i. Addition of small amount of acetanilide shows slow decomposition of hydrogen peroxide.

ii. Tetraethyl lead (TEL) acts as an antiknocking agent in the case of petrol. Thus, it decreases the knocking of petrol and acts as a negative catalyst.

iii. The oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3(s) + O_2(g) \xrightarrow{\text{Alcohol(l)}} 2Na_2SO_4(s)$$

iv. The oxidation of chloroform by air is retarded if some alcohol is added.

$$2CHCl_3(l) + O_2(g) \xrightarrow{\text{Alcohol(l)}} 2COCl_2(g) + 2HCl(g)$$

c. Auto-catalysis: In certain reactions, one of the products acts as a catalyst. In the initial stage the reaction is slow but as soon as products are formed, one of the products itself acts as a catalyst, and hence the reaction is known as auto-catalysis. For example:

i. When nitric acid is poured on copper, the reaction is very slow in the beginning. Gradually, the reaction becomes faster due to formation of nitrous acid during the reaction which acts as an auto-catalyst.

ii. In the hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an auto-catalyst in this reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

d. Induced catalysis: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions the phenomenon is known as induced catalysis.

Some examples are as follows:

i. Reduction of mercuric chloride ($HgCl_2$) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and mercuric chloride, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

ii. Sodium arsenite solution is not oxidized by air, if, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

Depending on whether a catalyst is in the same phase as the reaction mixture, catalysis is divided into two types:

a. Homogeneous catalysis: If a catalyst is present in the same phase as the reactants, it is called a homogeneous catalyst and this type of catalysis is called homogeneous catalysis. It is believed that in homogeneous catalysis, a catalyst enters into chemical combination with one or more of the reactants forming an intermediate compound which then decomposes or combines with one of the reactants to produce the product and the catalyst is regenerated.

A thoroughly studied example of homogeneous catalysis is the hydrolysis of organic ester (RCOOR′).

$$R{-}\overset{\overset{\ddot{O}:}{\|}}{C}{-}\ddot{O}{-}R'(l) + H_2O(l) \rightleftharpoons R{-}\overset{\overset{\ddot{O}:}{\|}}{C}{-}\ddot{O}H(l) + R'\ddot{O}H(l)$$

Here R and R' are alkyl groups, $R{-}\overset{\overset{\ddot{O}:}{\|}}{C}{-}\ddot{O}H$ is a carboxylic acid and $R{-}\ddot{O}H$ is an alcohol. The reaction rate is low at room temperature but can be increased by adding a small amount of a strong inorganic acid which provides $H^{\oplus}$ ions that acts as a catalyst in the reaction. Some other examples of homogeneous catalysis are:

i. Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

ii. Hydrolysis of methyl acetate is catalyzed by $H^{\oplus}$ ions furnished by hydrochloric acid

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and catalyst are in the same phase.

iii. Hydrolysis of sugar is catalyzed by $H^{\oplus}$ ions furnished by sulphuric acid

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H_2SO_4(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}}_{\text{Solution}}$$

iv. Catalytic decomposition of ozone by chlorine atoms in the gas phase

$$O_3(g) + O(g) \xrightarrow{Cl(g)} 2O_2$$

v. Oxidation of CO by O_2 in the presence of NO as catalyst

$$2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$$

b. Heterogeneous catalysis: When the catalyst is in different phase than the reactants, it is called heterogeneous catalyst, and this type of process is called heterogeneous catalysis.

In heterogeneous catalysis, the catalyst is generally a solid and the reactants are generally gases, but sometimes liquid reactants are also used. It is also known as surface catalysis, as the reaction starts at the surface of the solid catalyst. These catalysts have enormous surface areas between 1 and 500 $m^2\ g^{-1}$ for contact. Interestingly, many reactions that occur on a metal surface such as the decomposition of HI on gold and the decomposition of N_2O on platinum are zero order because the rate-determining step occurs on the surface itself. Thus, despite an enormous surface area, once the reactant gas covers the surface, it increases the rate of reaction.

One of the most important examples of heterogeneous catalysis is the addition of H_2 to the C=C bonds of organic compounds to form C—C bonds. This is known as catalytic hydrogenation reaction. The petroleum, plastics and food industries frequently use catalytic hydrogenation.

Examples of heterogeneous catalysis are given below:

i. Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactant is in gaseous state while the catalyst is in the solid state.

ii. Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

iii. Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

iv. Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst

$$\text{Vegetable oils}(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable ghee}(s)$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

Catalytic converter for an automobile

The catalytic converter in the car's exhaust which converts polluting exhaust gases into non-toxic ones contains a heterogeneous catalyst. In a single pass through the catalyst bed, CO and unburned petrol are oxidized to CO_2 and H_2O, while NO is reduce to N_2. Mixtures of transition metals and their oxides embedded in inert supports act as a catalyst.

$$2CO + O_2 \xrightarrow{\text{Catalyst}} 2CO_2$$

$$\underset{\text{(unburnt petrol)}}{\text{Hydrocarbons}} \xrightarrow[O_2]{\text{Catalyst}} CO_2 + H_2O$$

$$2NO \xrightarrow{\text{Catalyst}} N_2 + O_2$$

5.3.3 THEORIES OF CATALYSIS

There is no universal principle behind the action of catalysts as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. These are as follows:

a. Intermediate compound formation theory: It was proposed by Clement and Desormes in 1806. It successfully explains the homogeneous catalysis.

According to this theory, the catalyst first forms an intermediate compound with one of the reactants, which then decomposes or combines with another reactants to produce the product and the catalyst is regenerated. The catalyst in this reaction lowers the free energy of activation and hence accelerates the rate of reaction.

For example, the oxidation of SO_2 to SO_3 in the presence of NO takes place as follows:

$$\underset{\text{Reactant}}{O_2(g)} + \underset{\text{Catalyst}}{2NO(g)} \longrightarrow \underset{\text{Intermediate}}{2NO_2(g)}$$

$$\underset{\text{Reactant}}{SO_2(g)} + \underset{\text{Intermediate}}{NO_2(g)} \longrightarrow \underset{\text{Product}}{SO_3(g)} + \underset{\text{Regenerated Catalyst}}{NO(g)}$$

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction is effective in small quantities.

However, this theory is limited to homogeneous catalysis as the formation of intermediate compound is possible in the case of homogeneous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons, and action of finely divided catalyst.

b. Adsorption theory: This theory explains the mechanism of heterogeneous catalysis. According to the earlier adsorption theory of heterogeneous catalysis, it was believed that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilized in enhancing the rate of the reaction. This earlier theory does not explain the specificity of a catalyst.

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localized on the surface of the catalyst. The mechanism involves five steps:

- **i.** Diffusion of reactants to the surface of the catalyst
- **ii.** Adsorption of reactant molecules on the surface of the catalyst
- **iii.** Occurrence of chemical reaction on the catalyst's surface through the formation of an intermediate (Fig. 5.12)
- **iv.** Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur
- **v.** Diffusion of reaction products away from the catalyst's surface

The surface of the catalyst unlike the inner part of the bulk has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for fresh reactant molecules.

In case free valencies are responsible for the catalytic activity, it follows that with the increase of these valencies on the surface of a catalyst, the catalytic activity will be greatly enhanced. The free valencies can be increased in the following two ways:

1. By fine division of the catalyst
2. By rough surface of the catalyst

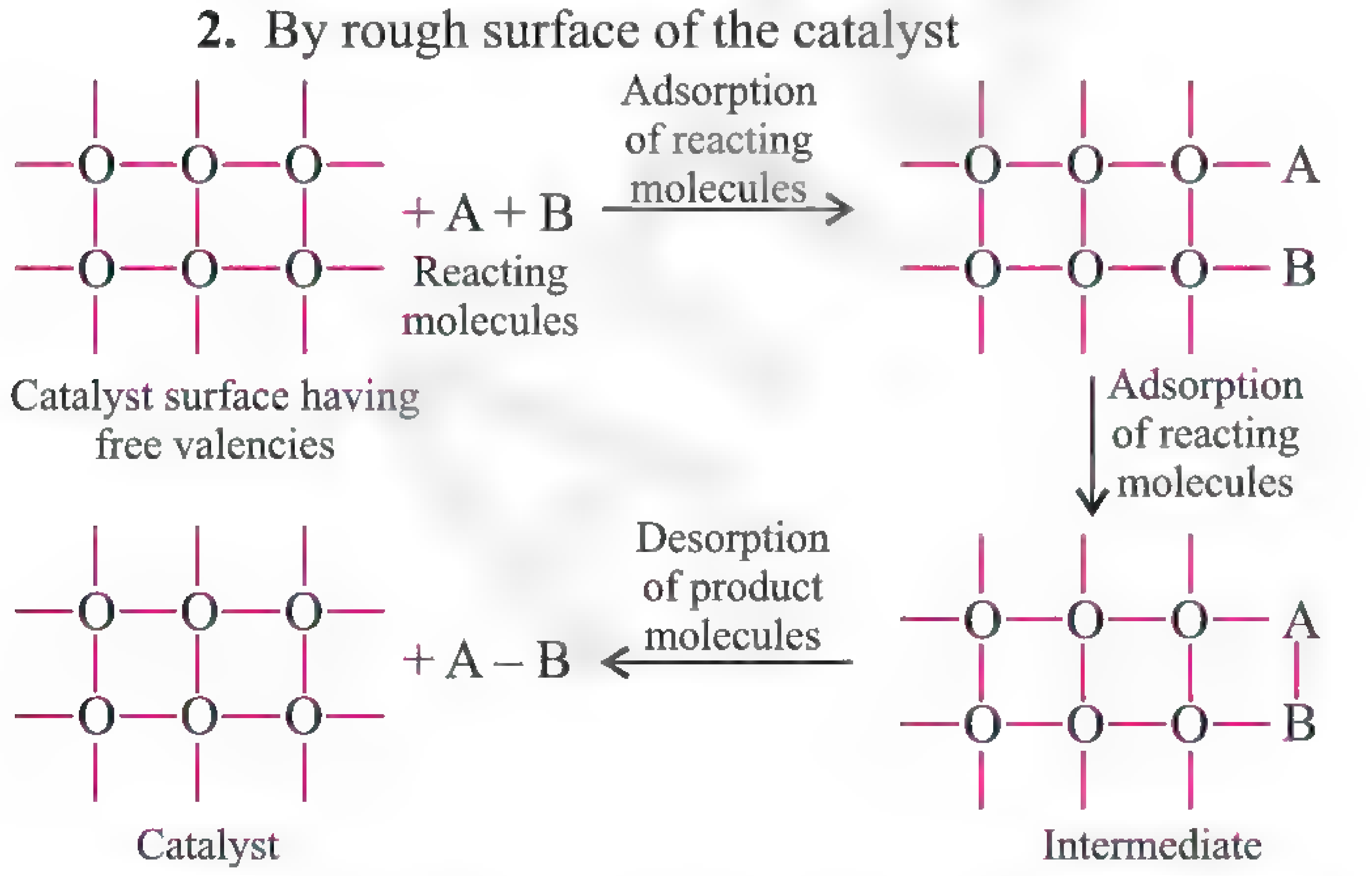


Fig. 5.12 Adsorption of reacting molecules, formation of intermediate, and desorption of products

This theory does not explain the action of catalytic promoters and catalytic poisons.

5.3.4 Important Features of Solid Catalysts (Heterogeneous Catalyst)

The effectiveness of a catalyst depends upon two important aspects: activity and selectivity.

a. Activity of a catalyst: Activity is the ability of a catalyst to accelerate the rate of a chemical reaction.

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactant must adsorb reasonably strongly for the catalyst to be active but must not adsorb so strongly that they become immobilize and the other reactants do not get space on the catalyst surface for adsorption. It has been observed that for hydrogenation, the catalytic activity increases as we go from Group 5 metals to Group 11 metals with maximum activity shown by elements of Group 7–9 in the periodic table.

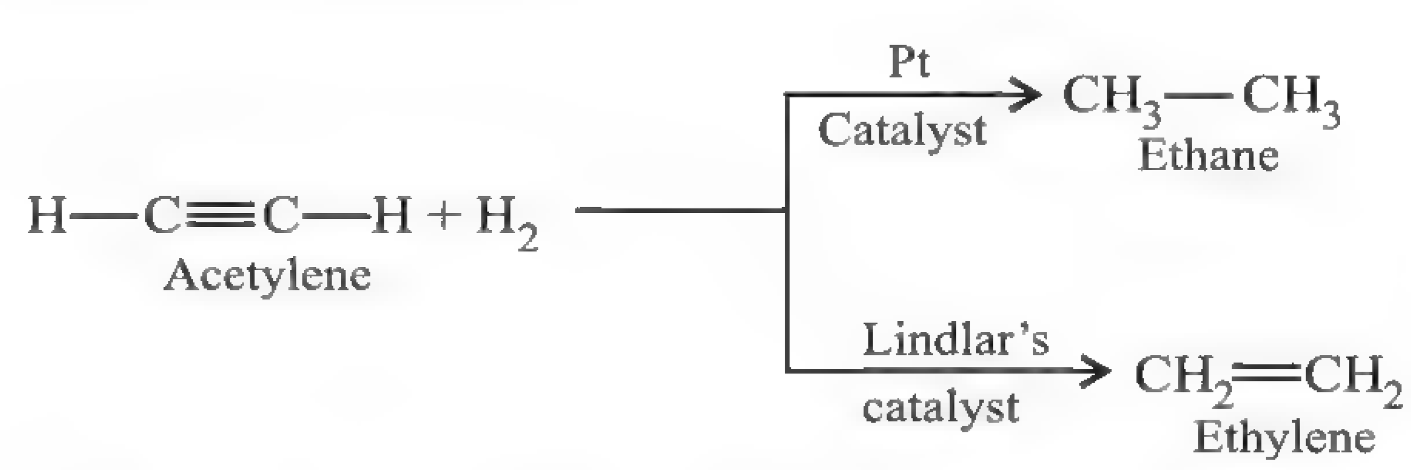
A catalyst may accelerate a reaction to as high as 10^{10} times. For example, the mixture of H_2 and O_2 can be stored for any period but in the presence of platinum, the reaction occurs with explosive violence.

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(g)$$

b. Selectivity of a catalyst: The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For examples, starting with H_2 and CO, and using different catalysts, we get different products.

- **i.** $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$
- **ii.** $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH(g)$
- **iii.** $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Similarly, acetylene on reaction with H_2 in the presence of Pt catalyst gives ethane, while in the presence of Lindlar's catalyst (palladium and $BaSO_4$ poisoned with quinoline or sulphur) gives ethylene.



Thus, it can be inferred that the action of a catalyst in highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means that a substance which acts as a catalyst in one reaction may fail to catalyze another reaction.

5.3.5 Shape-Selective Catalysis by Zeolites

Zeolites are naturally occurring or synthetic microporous aluminosilicates of general formula:

$M_{x/n}[(AlO_2)_x\,(SiO_2)_y]_m \cdot H_2O$

$M = Na^{\oplus}, K^{\oplus}$, or Ca^{2+}-like metals

n = Valency of metal cation

m = molecules of water of crystallization

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. Zeolites are aluminosilicates, i.e., three-dimensional network silicates in which some silicon atoms are replaced by aluminium atoms. They are found in nature as well as synthesized for catalytic selectivity. Zeolites, before using as catalyst, are heated in vacuum so that the water of hydration is lost. As a result, zeolites become porous, i.e., the cavities in the cage-like structure which were occupied by the water molecules become vacant. The size of the pores generally varies between 260 pm and 740 pm. Thus, only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily.

The reaction taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. That is why these types of reactions are called *shape-selective catalysis* reactions.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization. An important zelolite catalyst in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them so that a mixture of hydrocarbons is formed.

5.4 ENZYME CATALYSIS

Living organisms carry out thousands of chemical reactions which take place in dilute solution at ordinary temperature and pressure. For example, they can use small molecules to assemble complex biopolymers such as proteins and DNA. Organisms can produce molecules that combat bacterial invaders. They can break down large, energy-rich molecules in many steps to extract chemical energy in small portions to drive most of their activities.

Most of these reactions are catalyzed by biochemical catalysts called enzymes. Enzymes are proteins with high molar mass ranging from 15000 to 1000000 g mol^{-1}. Enzymes are incredibly efficient catalysts. They increase rates by 10^8 to 10^{20} times. Enzymes are also extremely specific: each reaction is generally catalyzed by a particular enzyme. Urease, for example, catalyzes only the hydrolysis of urea and none of the several thousand other enzymes present in the cell catalyzes that reaction.

$$NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + 2CO_2$$

Most enzymes have been obtained in pure crystalline state from living cell. However, the first enzyme was synthesized in the laboratory in 1969.

Following are some of the examples of enzyme-catalyzed reactions:

a. **Inversion of cane sugar:** The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

b. **Conversion of glucose into ethyl alcohol:** The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

c. **Conversion of starch into maltose:** The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(aq)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

d. **Conversion of maltose into glucose:** The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(aq)}$$

e. **Decompostion of urea into ammonia and carbon dioxide:** The enzyme urease catalyzes this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(g)$$

f. **Catalysis by pepsin and trypsin:** In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

g. **Conversion of milk into curd:** It is an enzymatic reaction brought about by lactobacilli enzyme present in curd.

Table 5.4 gives the summary of some important enzymatic reactions.

Table 5.4 Some enzymatic reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

5.4.1 Characteristics of Enzyme Catalysis

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

a. **High efficiency:** Enzymes are efficient catalyst. Even one molecule of an enzyme may transform one million molecules of the reactant per minute.

b. **High specificity:** The enzyme catalysts are highly specific in nature. Almost every biochemical reaction is controlled by its own specific enzyme, i.e., one enzyme cannot catalyze more than one reaction. For example, the enzyme urease catalyzes the hydrolysis of urea only. It does not catalyze hydrolysis of any other amide.

c. **Temperature dependence:** The rate of an enzyme reaction becomes maximum at a definite temperature, called the

optimum temperature. On either side of the optimum, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298–310 K. Human body temperature being 310 K is suited for enzyme-catalyzed reactions.

d. **pH dependence:** The rate of an enzyme-catalyzed reaction is maximum at a particular pH called optimum pH, which is lies between 5 and 7.

e. **Presence of activators and co-enzymes:** The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, catalytic activity is enhanced considerably.

   Activators are generally metal ions such as $Na^{\oplus}$, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride, i.e., $Na^{\oplus}$ ions, is catalytically very active.

f. **Influence of inhibitors and poisons:** Like ordinary catalysis, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduced or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

5.4.2 Mechanism of Enzyme Catalysis

The remarkable specificity of enzymes results from the fact that each enzyme has a specific, active site on its surface such as —NH_2, —COOH, —SH, —OH, etc. These are actually the active centres on the surface of enzyme particles; when the reactant molecules, called the substance of the reaction, bind at the active site, a chemical change is initiated and an activated complex is formed which then decomposes to yield the products. In most cases, the substrate binds to the active site through intermoleuclar forces: H-bonds, dipole forces, and other weak attractions.

Two models of enzyme action have been proposed (Fig. 5.13):

a. Lock and key model   b. Induced fit model

According to the *lock and key model*, every lock (active site) has a particular shape and when a particular key (substrate), which has complementary shape, fits into a lock, the chemical change begins, which finally results into a product (Fig. 5.13).

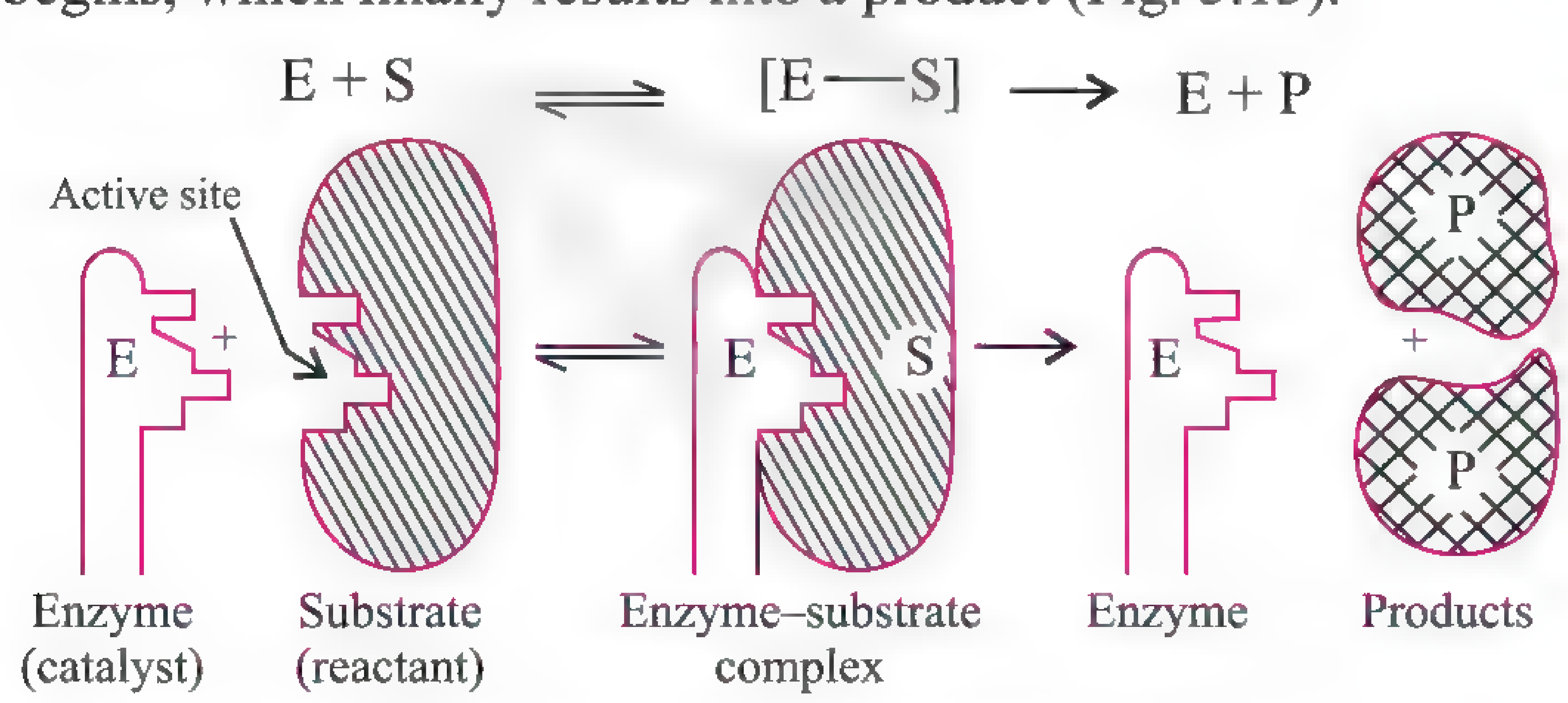


Fig. 5.13 Mechanism of enzyme-catalyzed reaction

Modern X-ray crystallographic and spectroscopic methods have shown that in many cases, unlike an ordinary lock, the protein molecules (enzyme) slightly change the shape when a substrate lands at the active site. The ability of an enzyme to undergo the correct distortion also determines whether the "key" will fit or not. This refinement of the original lock-and-key model is known as *induced fit model*. According to this model, a substrate induces the active site to adopt a perfect fit rather than a rigidly shaped lock and key. Therefore, we can picture this model as *hand in a glove*, in which the glove (active site) does not attain its functional shape until the hand (substrate) moves into place.

The kinetics of enzyme catalysis has many features in common with ordinary catalysis. In the enzyme-catalyzed reaction, substrate (S) and enzyme (E) form an intermediate enzyme-substrate complex (ES) whose concentration determines the rate of product (P) formation. The steps common to virtually all enzyme-catalyzed reactions are:

Step 1: Binding of enzyme to substrate to form an activated complex.

$$E + S \longrightarrow ES^{\neq} \qquad \text{(Fast, reversible)}$$

Step 2: Decomposition of the activated complex to form product.

$$ES^{\neq} \longrightarrow E + P \qquad \text{(Slow, rate determining)}$$

The rate of enzyme-catalyzed reaction changes from first order to zero-order as the concentration of substrate is increased.

5.4.3 Catalysts in Industry

The enzymes are widely used in industrial processes. Some of the important catalytic processes are listed in Table 5.5 to give an idea about the utility of catalysts in industries.

Table 5.5 Some industrial catalytic processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; condition: 200 bar pressure and 723–773 K temperature. Now-a-days, a mixture of iron oxide, potassium oxide, and alumina is used.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$; $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinized asbestos: temperature 573 K
3. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; $SO_3(g) + H_2SO_4(aq) \rightarrow \underset{\text{Oleum}}{H_2S_2O_7(aq)}$; $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinized asbestos or vanadium pentoxide (V_2O_5): temperature 673–723 K.

ILLUSTRATION 5.22

Why is it necessary to remove CO when ammonia is obtained by Haber's process?

Sol. CO acts as a poison for the catalyst used in the manufacture of ammonia by Haber's process. Hence, it is necessary to remove it.

ILLUSTRATION 5.23

Why is ester hydrolysis slow in the beginning and becomes faster after some time?

Sol. The ester hydrolysis takes place as follows:

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Water}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

The acid produced in the reaction acts as catalyst (autocatalyst) for the reaction. Hence, the reaction becomes faster after some time.

ILLUSTRATION 5.24

What do you mean by activity of catalysts?

Sol. Activity is the ability of catalysts to accelerate chemical reactions.

ILLUSTRATION 5.25

How does BF_3 act as a catalyst in industrial process?

Sol. BF_3 is a strong Lewis acid. Hence, it is used as a catalyst in industrial processes.

ILLUSTRATION 5.26

Give an example of a shape-selective catalyst.

Sol. Zeolites are shape-selective catalysts. A zeolite called ZSM-5 converts alcohol to gasoline.

ILLUSTRATION 5.27

Explain the shape-selective catalysis.

Sol. The catalytic reaction which depends upon the pore size of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honey comb like structures. ZSM-5 is used in petroleum industry to convert alcohols directly into gasoline by dehydrating them to give a mixture of hydrocarbons.

$$xCH_3\text{—}OH \xrightarrow{\text{ZSM-5}} \underset{\text{Gasoline}}{(CH_2)_x} + xH_2O$$

ILLUSTRATION 5.28

What is the role of desorption in the process of catalysis?

Sol. Desorption makes the surface of a solid catalyst free for fresh adsorption of reactants on the surface.

ILLUSTRATION 5.29

i. The ability of a catalyst to direct the reaction to yield particular products is called

a. Reactivity **b.** Selectivity **c.** Activity **d.** Fugacity

ii. Which of the following is an example of zeolite?

a. ZSM-5 **b.** $AgNO_3$ **c.** $Mg(OH)_2$ **d.** $Co(OH)_3$

iii. Reactions in zeolite catalyst depend on

a. Pores **b.** Apertures

c. Size of cavities **d.** All of these

Sol. **i. b.** **ii. a.** **iii. d.**

ILLUSTRATION 5.30

Taking two examples of heterogeneously catalyzed reactions, explain how a heterogeneous catalyst helps in the reaction.

Sol. Solid catalysts are used in a number of gaseous reactions. Such catalytic reactions are called heterogeneous reactions. Examples of heterogeneous catalysis are as follows:

a. Manufacture of ammonia from N_2 and H_2 by Haber's process in the presence of catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

b. V_2O_5 catalyst is used in the manufacture of H_2SO_4 by contact process.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

Solid catalyst helps in the following ways:

i. Simultaneous adsorption of reactants increases with concentration at the surface of the catalyst which increases the reaction rate.

ii. Adsorption of reactant molecules makes the attack of other molecules on it easier.

iii. Some adsorbed molecules dissociate into atoms which are very reactive.

iv. The heat of adsorption released provides activation energy for the reaction.

ILLUSTRATION 5.31

Give four examples of heterogeneous catalytic reactions.

Sol.

a. Contact process reactions

b. Haber's process reactions

c. Hydrogenation of vegetable oils

$$\text{Vegetable oil} + H_2 \xrightarrow{Ni} \text{Vegetable ghee}$$

$$CH_2=CH_2 + H_2 \xrightarrow{Ni} CH_3\text{—}CH_3$$

d. Synthesis of methanol

$$CO(g) + 2H_2(g) \xrightarrow{Cu,\ ZnO-Cr_2O_3} CH_3OH\ (l)$$

ILLUSTRATION 5.32

How does the rate of an enzyme-catalyzed reactions vary with (a) temperature and (b) pH? Represent diagrammatically.

Sol. As the temperature or pH is increased, the rate rises till it is maximum at 37°C (physiological temperature) or pH = 7.4 and then falls off (as shown in the figure).

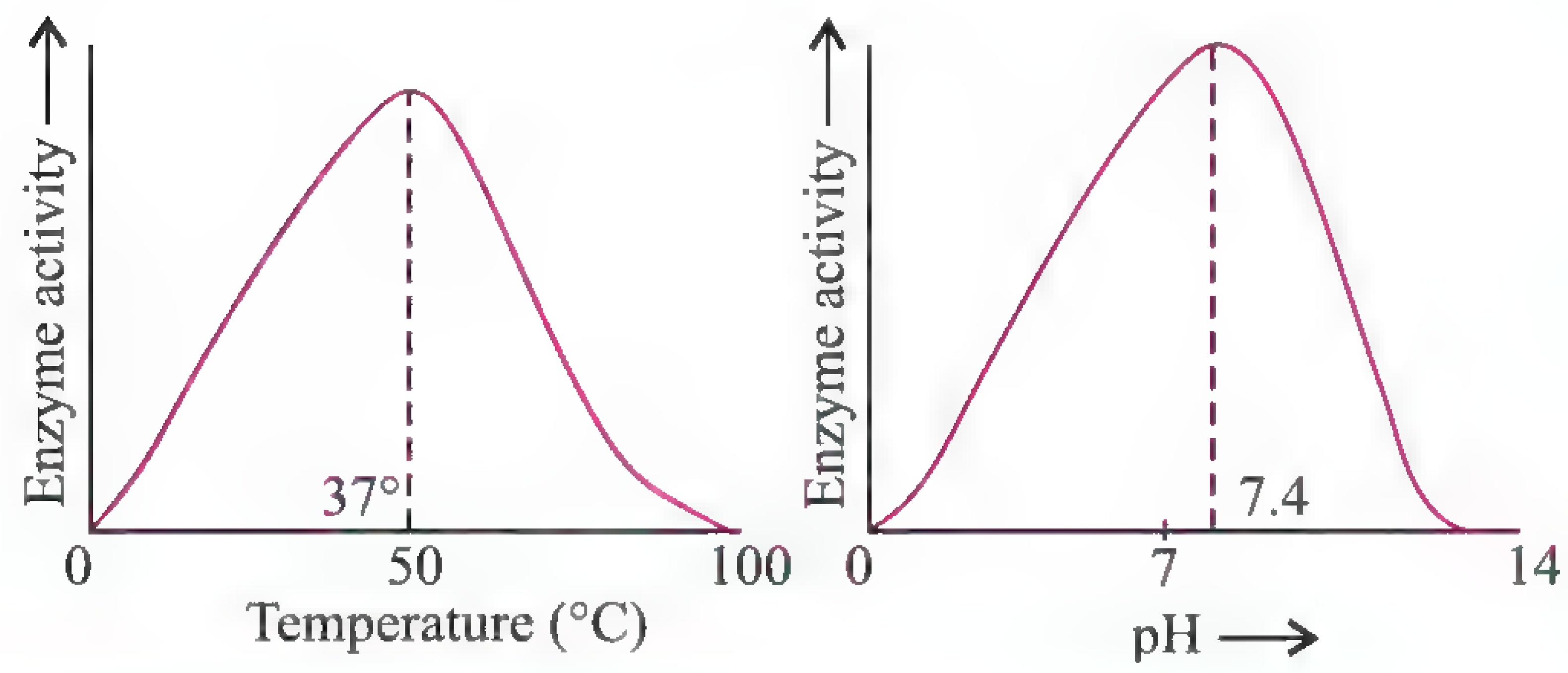


ILLUSTRATION 5.33

Indicate a chemical reaction involving a homogeneous catalyst.

Sol. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

ILLUSTRATION 5.34

How does a catalyst work?

Sol. It provides an alternate path involving lower activation energy for the reactants.

ILLUSTRATION 5.35

What do you mean by activity and selectivity of catalyst?

Sol. Activity is the ability of a catalyst to accelerate chemical reactions, for example, Pt catalyzes the combination of H_2 and O_2 to form water. It has been found that for hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by Group 7–9 elements of the periodic table.

Selectivity is the ability of a catalyst to direct a reaction to yield a particular product. A combination of CO and H_2 yields different products with different catalysts as given below:

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$$

$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

ILLUSTRATION 5.36

i. Which of the following small-sized elements can replace silicon and aluminium in the framework at zeolites

a. Boron **b.** Magnesium
c. Phosphorus **d.** All

ii. Zeolites are microporous aluminosilicates with general formula

a. $M[(AlO_2)_x]\cdot mH_2O$
b. $M_x[(AlO_2)_x(SiO_2)_y]$
c. $M_x[(SiO_2)_y]\cdot mH_2O$
d. $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot mH_2O$

iii. The zeolites have shape selectivity depending on

a. Pore structure **b.** Atomic structure
c. Molecular structure **d.** None

Sol.

i. d **ii. d** **iii. a**

ILLUSTRATION 5.37

A catalyst lowered the activation energy by 25 kJ mol^{-1} at 25°C. By how many times will the rate grow?

Sol. The rate of reaction is related to the activation energy by the following relation:

$$\frac{K_2}{K_1} = \text{Antilog}\left[\frac{\Delta E}{2.303RT}\right] \qquad ...(i)$$

Given, $\Delta E = 25 \times 10^3$ J

$R = 8.314$ J K^{-1} mol^{-1}

$T = 25°C = 298$ K

Substituting all the values in Eq. (i), we get

$$\frac{K_2}{K_1} = \text{Antilog}\left[\frac{25\times10^3}{2.303\times8.314\times298}\right] = 24069$$

$\therefore K_2 = K_1 \times 24069$

Therefore, the rate increases by 24069 times.

ILLUSTRATION 5.38

At 400 K, the energy of activation of a reaction is decreased by 0.8 kcal in the presence of catalyst. Hence, the rate will be

a. Increased by 2.73 times
b. Increased by 1.18 times
c. Decreased by 2.72 times
d. Increased by 6.26 times

Sol.

a. We know

$$\frac{K_2}{K_1} = \text{Antilog}\left[\frac{\Delta E}{2.303RT}\right] \qquad ...(i)$$

Given $\Delta E = 0.8$ kcal $= 3.344 \times 10^3$ J

$R = 8.314$ J K^{-1} mol^{-1}

$T = 400$ K

Substituting all the values in Eq. (i), we get

$$\frac{K_2}{K_1} = \text{Antilog}\left[\frac{3.344\times10^3}{8.314\times2.303\times400}\right] = 2.73$$

$\therefore K_2 = 2.73\ K_1$

Therefore, the rate will increase by 2.73 times.

5.5 COLLOIDS

The foundation of colloidal chemistry was laid down by an English scientist, Thomas Graham, in 1861.

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane, whereas others do not diffuse at all. The former type of substances on account of their crystalline nature such as common salt, sugar, urea, etc., were named crystalloids while the latter type were termed as colloids (Greek word, *kola*, meaning glue-like). All inorganic acids, bases, and salts and organic compounds such as sugar, urea, etc., were included in crystalloids while substances such as starch, gelatine, gums, silicic acid, etc., belonged to the colloidal group.

It was soon realized that the above classification was not perfect since many crystalline substances can be converted into colloidal form by suitable means. The colloidal form of sodium chloride, a crystalloid, can be obtained in benzene. Thus, the above classification was discarded, i.e., the term colloid does not apply to a particular class of substances but is a state of matter such as solid, liquid, and gas. Any substance can be brought into colloidal state by suitable means. Therefore, there is no separate class of substances called colloidal substance. It is just a state of matter into which every substance can be obtained by a suitable method. Further studies of the behaviour of these solutes have shown that the nature of a substance whether crystalloid or colloid depends upon the size of the solute particles. When the size of the solute particles lies between 1 nm and 100 nm it behaves like a colloid. If the size of solute particles is greater than 100 nm, it exists as suspension, and if the particle size is less than 1 nm, it exists as a true solution.

Thus, a colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. In a colloid, the dispersed phase may consist of particles of a single macromolecule (such as synthetic polymer or protein) or an aggregate of many atoms, molecules, or ions.

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm^2. If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60000 cm^2 or 6 m^2. This enormous surface area leads to some special properties of colloids to be discussed later in this chapter.

The distinction between characteristics of suspension, colloidal solution, and true solution is tabulated in Table 5.6.

Table 5.6 Difference between suspension, colloidal solution, and true solution

S.No.	Property	True solution	Colloidal solutions	Suspension
1.	Particle size	Less than 10^{-9} m or 1 nm (i.e., <10 Å)	Between 10^{-9} and 10^{-7} m or 1 nm and 100 nm	More than 10^{-7} m or 100 nm (i.e., >1000 Å)
2.	Filterability	Pass through ordinary filter paper as well as animal membrane	Pass through ordinary filter paper but not through animal membrane	Do not pass through filter paper as well as animal membrane
3.	Settling	Do not settle	Do not settle	Settle on standing
4.	Visibility	Particles are invisible	Scattering of light by the particles is observed under ultra-microscope.	Particles are visible to naked eye or under a microscope.
5.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse
6.	Appearance	Clear and transparent	Transluscent	Opaque

5.5.1 Classification of Colloids

Colloids are classified on the basis of following criteria:

a. Physical state of dispersed phase and dispersion medium
b. Nature of interaction between dispersed phase and dispersion medium
c. Type of particles of the dispersed phase

Colloidal solution is heterogeneous in nature and always consists of at least two phases, namely, disperse phase and dispersion medium. The component present in small proportion and consisting of particles of colloidal dimensions is called *disperse phase*. The medium in which colloidal particles are dispersed is called *dispersion medium*.

Classification Based on the Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids, or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 5.7.

It is clear from Table 5.7 that many common commercial products and natural objects are colloids. For example, whipped cream is a colloidal system (foam), a gas dispersed in a liquid. Out of the different types of colloids, the most common are *sols* (solids in liquids), *gels* (liquids in solids), and *emulsions* (liquids in liquids).

Table 5.7 Types of colloidal system

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example:

Dispersion medium	Name of colloidal solution
Water	Hydrosols
Alcohol	Alcosols
Benzene	Benzosols
Air	Aerosols

Classification Based on the Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, *lyophilic* (solvent attracting) and *lyophobic* (solvent repelling). If water is a dispersion medium, the terms used are hydrophilic and hydrophobic.

a. **Lyophilic colloids:** The word *lyophilic* means liquid-loving. Colloidal sols directly formed by mixing substances such as gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. As they form the colloidal sol directly they are also called intrinsic colloids. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called *reversible sols*. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.

b. **Lyophobic colloids:** The word *lyophobic* means liquid-hating. Substances such as metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols. As their colloidal sols have to be prepared by indirect methods, they are also called extrinsic colloids. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and, hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called *irreversible sols*. Lyophobic sols need stabilizing agents for their preservation.

The essential difference between lyophilic sols and lyophobic sols are given in Table 5.8.

Table 5.8 Difference between lyophilic sols and lyophobic sols

S. No.	Property	Lyophilic sol	Lyophobic sols
1.	Ease of preparation	Prepared easily by directly mixing with the liquid dispersion medium.	Cannot be prepared directly. Prepared by special methods only.
2.	Stability	They are quite stable and are not easily precipitated or coagulated.	They are easily precipitated by addition of a small amount of a suitable electrolyte.
3.	Reversible and irreversible nature	They are reversible in nature, i.e., once precipitated can reform the colloidal solution by simply remixing with the dispersion medium.	They are irreversible in nature, i.e., once precipitated cannot form the colloidal solution by simple addition of the dispersion medium.
4.	Nature of substances	These sols are usually formed by organic substances such as starch, gum, proteins, etc.	These sols are usually formed by inorganic materials such as metals, their sulphides, etc.

5.	Viscosity	Their viscosity is much higher than that of the medium.	Their viscosity is almost the same as that of the medium.
6.	Surface tension	Their surface tension is usually lower than that of the dispersion medium.	Their surface tension is nearly same as that of the dispersion medium.
7.	Visibility	Their particles are neither visible nor detected easily by an ultra-microscope (by the scattering of light).	Their particles, though not visible, can be easily detected by an ultra-microscope.
8.	Migration in an electric field	Their particles may migrate in either direction or may not migrate at all.	Their particles migrate in only one particular direction in the electric field.

Classification Based on the Type of Particles of the Dispersed Phase

Depending upon the type of particles of the dispersed phase, the colloids are classified as:

a. Multimolecular colloids
b. Macromolecular colloids
c. Associated colloids

a. Multimolecular colloids: When on dissolution a large number of atoms or smaller molecules of a substance (with diameter less than 1 nm) aggregate together to form species having size falling in the colloidal range, the species thus formed are called multimolecular colloids. The dispersed phase in this type of colloidal system may contain large aggregates of atoms of molecules formed as a result of aggregating properties of the dispersing particles. For example, a gold sol may contain particles of various sizes having several atoms. Sulphur sol consists of particles containing a thousand or so of S_8 sulphur molecules. These are held together by van der Waals forces.

b. Macromolecular colloids: When certain substances having big size molecules, called macromolecules having large molecular masses, are dissolved in a suitable liquid, they form a solution in which the molecules of the substance, i.e., the dispersed particles, have size falling in the colloidal range. Such substances are called macromolecular colloids.

The macromolecular substances are usually polymers with very high molecular masses. Examples of naturally occurring macromolecules are starch, cellulose, proteins, enzymes, and gelatin.

Examples of man-made macromolecules are polyethylene, nylon, polystyrene, synthetic, rubber, etc. As these molecules have large sizes and have dimensions comparable to those colloidal particles, their dispersions are called macromolecular colloids. Their colloidal solutions are quite stable and resemble true solutions in many respects.

c. Associated colloids (micelles): There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids. *The formation of micelles takes place only above a particular temperature called Kraft temperature (T_K) and above a particular concentration called critical micelle concentration (CMC).* On dilution, these colloids revert back to ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation

Micelles are generally formed by the aggregation of several ions or molecules with lyophilic as well as lyophobic parts. Let us take the example of soap solutions. Soap is a sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^{\ominus}N^{\oplus}$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^{\ominus}Na^{\oplus}$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^{\ominus}$ and $Na^{\oplus}$ ions. The $RCOO^{\ominus}$ ions, however, consist of two parts—a long hydrocarbon chain R (also called non-polar "tail") which is hydrophobic (water repelling), and a polar group $COO^{\ominus}$ (also called polar-ionic "head"), which is hydrophilic (water loving).

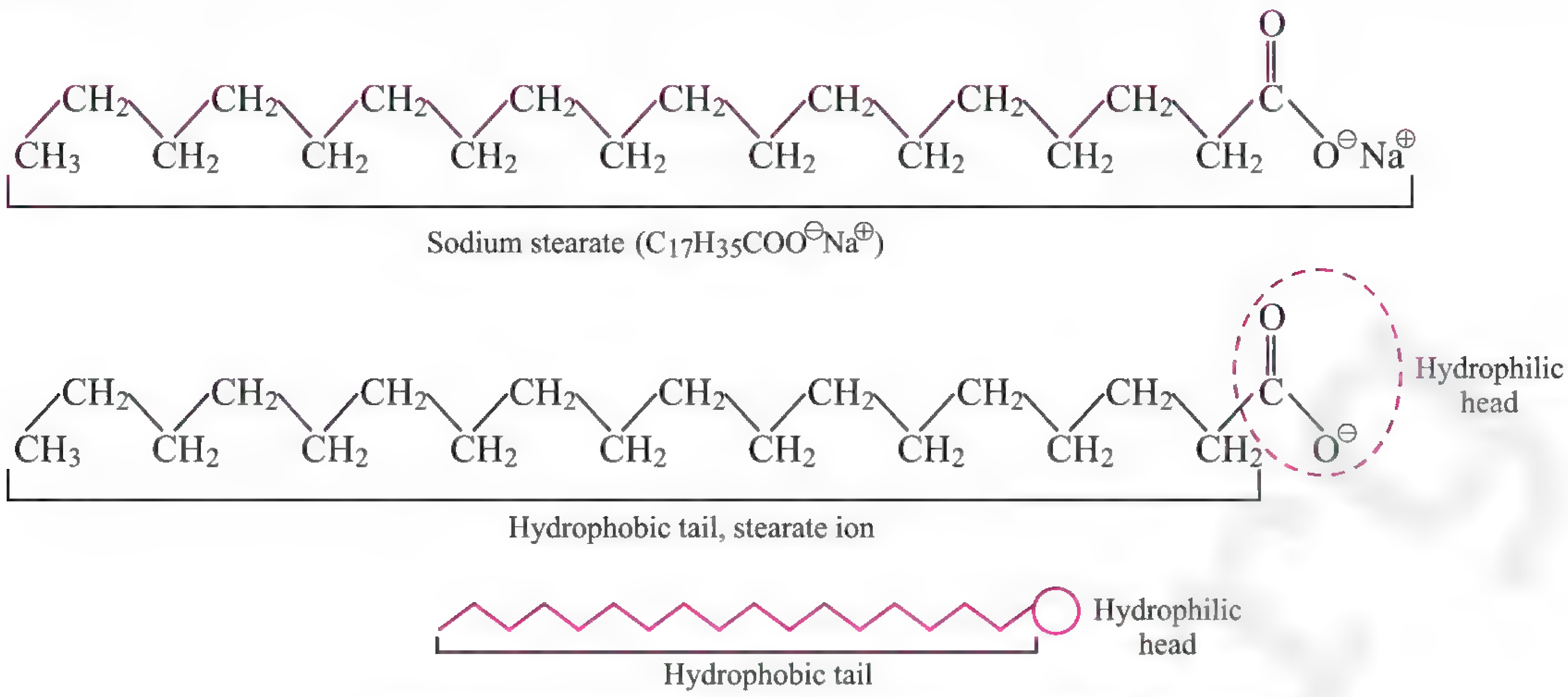


Fig. 5.14 Hydrophobic and hydrophilic parts of stearate ion

The $RCOO^{\ominus}$ ions are, therefore, present on the surface with their $COO^{\ominus}$ groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with $COO^{\ominus}$ part remaining outward on the surface of the sphere. An aggregate thus formed is known as *ionic micelle*. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents. e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4{}^{\ominus}Na^{\oplus}$, the polar group is $-SO_4{}^{\ominus}$, along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

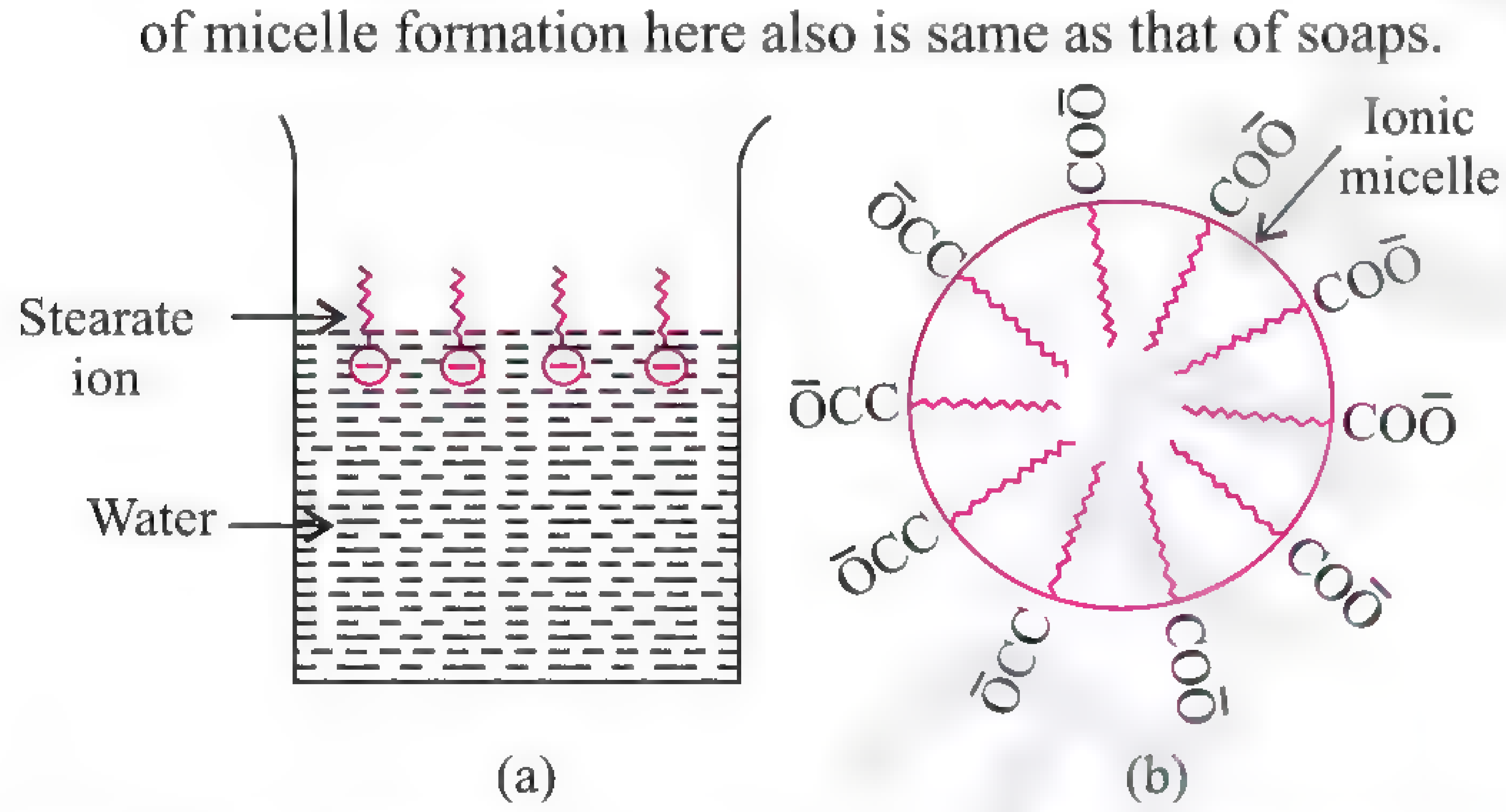


Fig. 5.15 (a) Arrangement of stearate ions on the surface of water at low concentrations of soap
(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

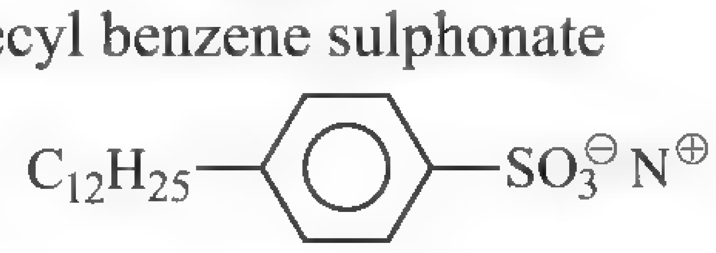
Some other examples of micelle systems are as follows:

i. Sodium lauryl sulphonate $CH_3[CH_2]_{11}\ SO_3{}^{\ominus}Na^{\oplus}$

ii. Sodium oleate $C_{17}H_{33}COO^{\ominus}Na^{\oplus}$

iii. Cetyl trimethyl ammonium bromide $CH_3(CH_2)_{15}N^{\oplus}(CH_3)_3Br^{\ominus}$

iv. *p*-Dodecyl benzene sulphonate



Cleansing action of soaps

The cleansing action of soap is due to the fact that soap molecules form micelles around the oil droplet in such a way that the hydrophobic part of stearate ions is in the oil droplet and the hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.16).

When a piece of cloth is dipped in aqueous soap solution, the soap and the dirt come in contact with each other. The non-polar end (tail) dissolves in the grease deposit while the polar end (—$COO^{\ominus}$ or head) is directed towards water. In this manner, each oil droplet is surrounded by a number of negatively charged carboxylate ions. Since similar charges repel each other, the oil droplets break up and form small droplets. These small droplets get dispersed in water forming an emulsion. The hand rubbing or the agitation due to washing machine causes dispersion of the oil or grease throughout the soapy water. These are washed away with water along with dust particles. In this way grease or dirt are removed from the surface of the cloth.

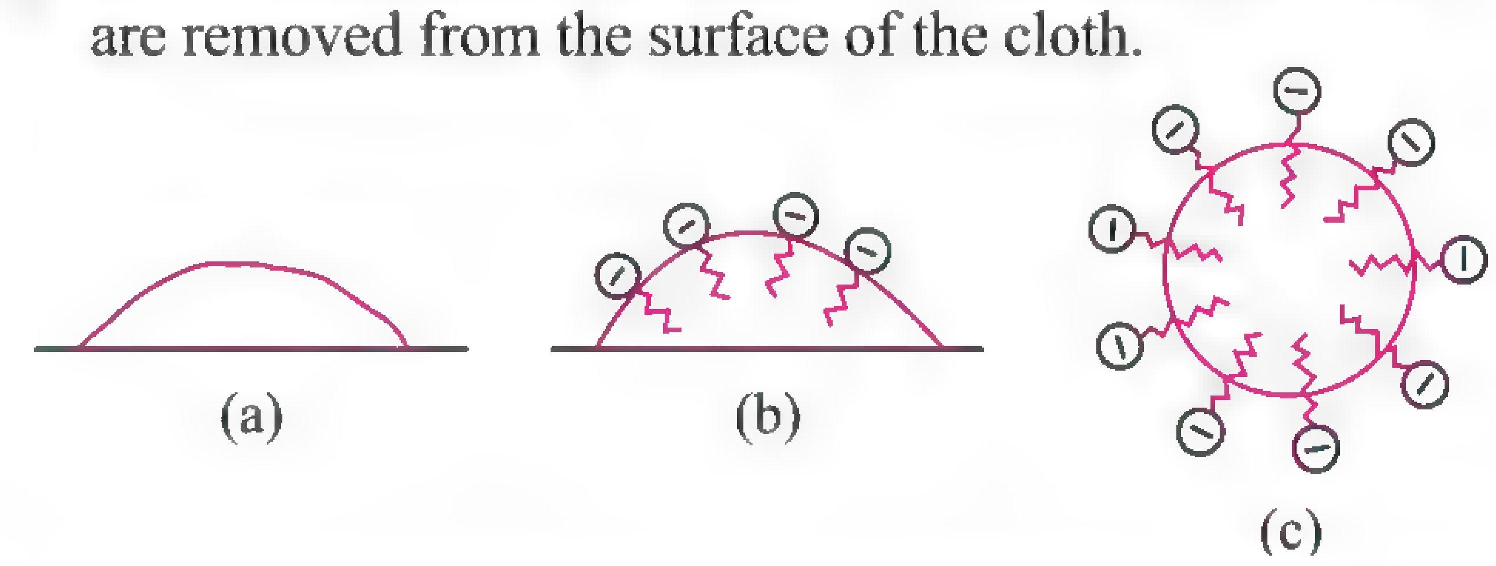


Fig. 5.16 (a) Grease on cloth, (b) stearate ions arranging around the grease droplet, and (c) grease droplet surrounded by stearate ions (micelle formed)

The important differences between multimolecular, macromolecular, and associated colloids are listed in Table 5.9.

Table 5.9 Differences between multimolecular, macromolecular and associated colloids

Multimolecular colloids	Macromolecular colloids	Associated colloids
1. They consist of aggregates of atoms or molecules which generally have diameter less than 1 nm.	They consist of large molecules (generally polymers)	They behave as colloidal size particles at higher concentrations.
2. The atoms or molecules are held by weak van der Waals forces.	The molecules are flexible and can take any shape.	They behave as normal electrolytes at low concentrations.
3. They have usually lyophilic character.	They have usually lyophobic character.	Their molecules contain both lyophilic and lyophobic groups.

5.5.2 Preparation of Colloidal Solutions

Lyophilic and lyophobic colloidal solutions (or sols) are generally prepared by different types of methods. Some of the common methods are as follows:

a. **Preparation of lyophilic sols:** The lyophilic sols can be prepared directly by mixing a substance with a dispersion medium. For example, colloidal sols of starch, gelatin, gum arabic, soaps, etc., are prepared by simply dissolving these substances in warm water. Similarly, a colloidal sol. of cellulose nitrate is obtained by dissolving it in an organic solvent such as ethyl alcohol. The product obtained is called collodion.

b. **Preparation of lyophobic sols:** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension (1 Å to 10^3 Å) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which lyophobic sols can be prepared.

   i. **Dispersion methods:** By splitting coarse aggregates of a substance into colloidal size.

   ii. **Condensation methods:** By aggregating very small particles (atoms, ions, or molecules) into colloidal size.

   i. **Dispersion or disintegration methods:** The methods involves the breaking of bigger particles into colloidal size. The methods generally employed for this purpose are briefly described below.

   1. **Mechanical disintegration:** The mechanical disintegration is carried out in a machine called colloid mill. It consists of two steel discs with a little gap in-between and capable of rotating in the opposite direction at a very high speed (about 7000 revolutions per minute). Solid material is first finely ground by usual method.

      It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

Note:

- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.
- This method comprises both dispersion and condensation.

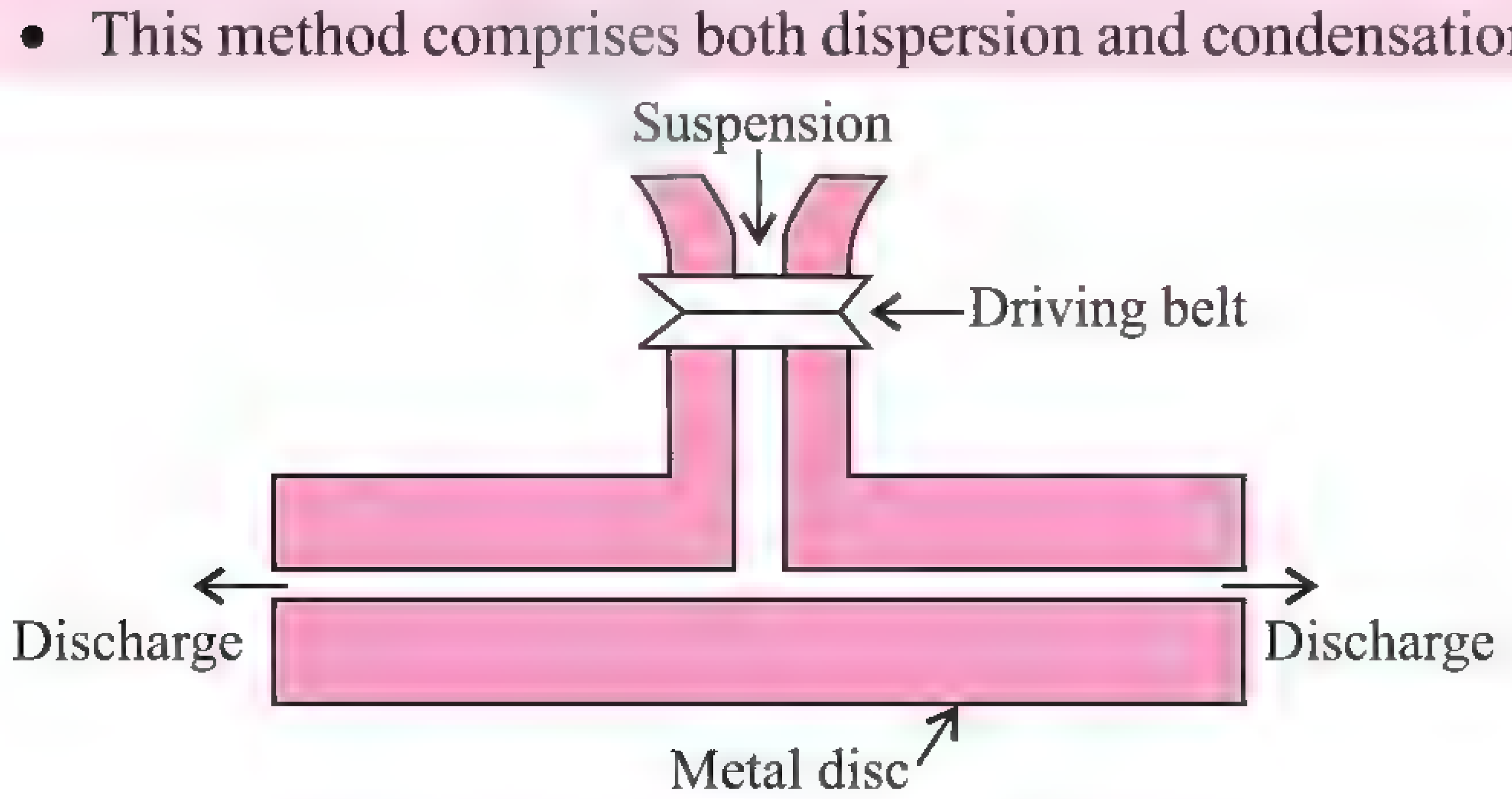


Fig. 5.17 Colloidal mill

2. **Electrical disintegration or Bredig's Arc method:** This method is employed for obtaining colloidal solutions of metal such as gold, silver, platinum, etc. In this method, an electric arc is struck between two metallic electrodes, immersed in the dispersion medium (Fig. 5.18). The intense heat produced vapourizes some of the metal, which then condenses to form particles of colloidal size. The colloidal solution prepared is stabilized by adding a small amount of KOH to it. This process involves dispersion as well as condensation.

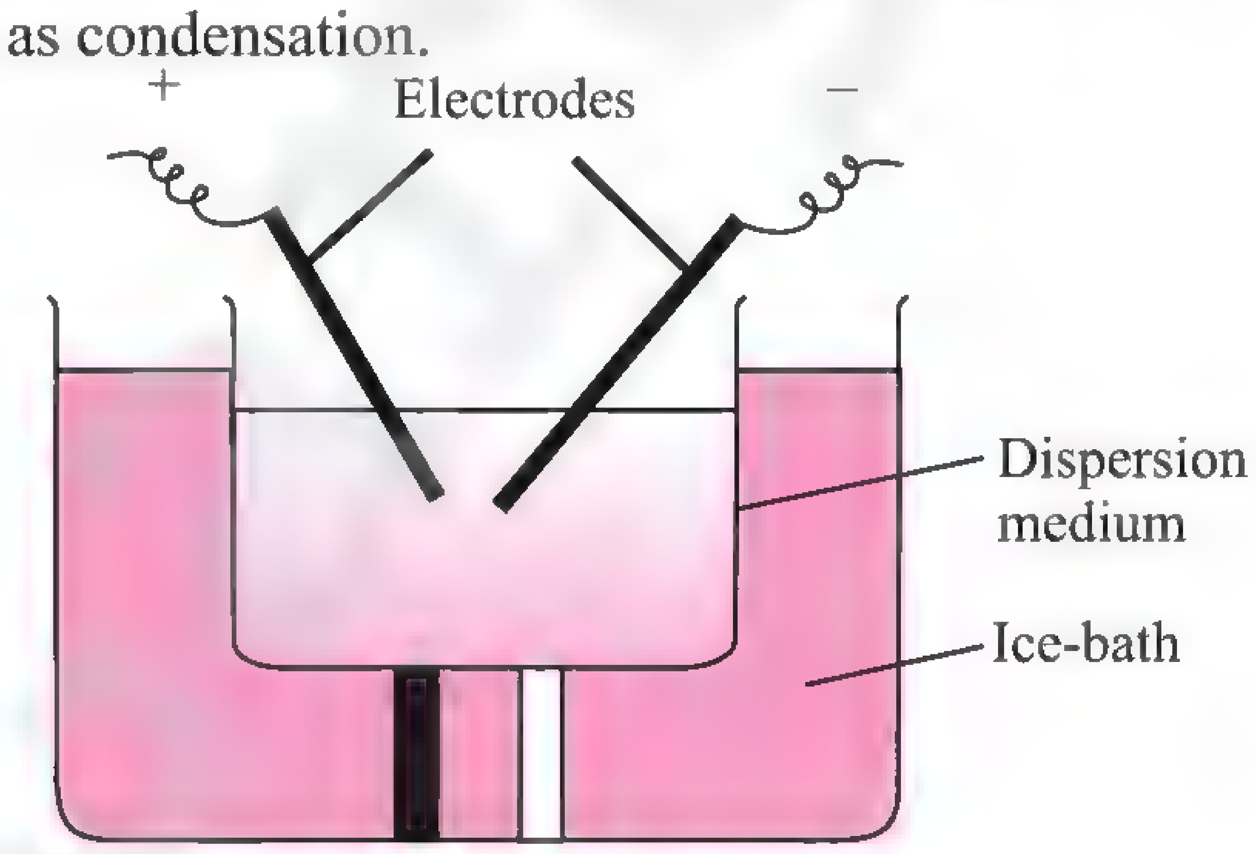


Fig. 5.18 Bredig's arc method

3. **Peptization:** Peptization may be defined as the *process of converting a precipitate into colloidal sol* by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called *peptizing agent.* This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

   A few examples of sols obtained by peptization are given below:

   - A reddish brown coloured colloidal solution is obtained by adding small quantity of ferric chloride solution to the freshly precipitated ferric hydroxide.
   - A precipitate of silver iodide can be peptized by shaking with a dilute solution of silver nitrate or KI.
   - On adding insufficient quantity of very dilute HCl solution to the freshly precipitated aluminium hydroxide, a sol of aluminium hydroxide is obtained.

   Causes of peptization: During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of precipitate. This causes the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions. For example, when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent), it adsorbs Fe^{3+}. Similarly, a precipitate of AgCl on shaking with dilute solution of $AgNO_3$ adsorbs $Ag^{\oplus}$ ion and get peptized to colloidal particles of the type $[AgCl]Ag^{\oplus}$. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptized by ethanol. The colloidal solution of cellulose nitrate in ethanol is called colloidion.

ii. Condensation method: In these methods, smaller particles of dispersed phase are condensed suitably to be colloidal size. This is done by the following methods:

1. **By exchange of solvent:** If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.
2. **By change of physical state:** Colloidal solutions of certain elements such as mercury and sulphur are obtained, passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).
3. **Chemical methods:** The chemical method involves chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided.
   - **Double decomposition:** A colloidal solution of arsenic sulphide is obtained by passing hydrogen sulphide into a solution of arsenic oxide in distilled water.
     $As_2O_3 + 3H_2O \longrightarrow As_2S_3 \text{ (yellow sol)} + 3H_2O$
     Sols of silver halide are obtained by mixing dilute solutions of silver salts and alkali metal halides in equivalent amounts.
     $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
   - **Oxidation:** A colloidal solution of sulphur can be prepared by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidizing agent such as bromine water or nitric acid.
     $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S \text{ (sol)}$
     Sulphur sol can also be obtained when H_2S is bubbled through an oxidizing agent (bromine water or nitric acid).
   - **Reduction:** A colloidal solution of a metal such as silver, gold, or platinum can be prepared by the reduction of its salt solution with a suitable reducing agent such as stannous chloride, formaldehyde, hydrazine, etc.
     $2AuCl_3 + 3SnCl_2 \longrightarrow 2Au \text{ (Gold sol)} + 3SnCl_4$
     $4AgCl + N_2H_4 \longrightarrow 4Ag \text{ (Silver sol)} + N_2 + 4HCl$
     $2PtCl_4 + 4SnCl_2 \longrightarrow 4SnCl_4 + 2Pt\text{(sol)}$
   - **Hydrolysis:** By this method hydroxide sols of less electropositive metals such as Fe, Al, or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.
     $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 \text{ (Red sol)} + 3HCl$

5.5.3 Purification of Colloidal Solutions

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods:

a. **Dialysis:** The process of separating the particles of colloid from those of crystalloids by means of diffusion through a suitable membrane is called dialysis. Its principle is based upon the fact that colloidal particles cannot pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it. The colloidal solution is taken in a bag made of cellophane or parchment. The bag is suspended in fresh water. The impurities slowly diffuse out of the bag leaving behind pure colloidal solution. The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag. Dialysis can be used for removing HCl from the ferric hydroxide sol. The method is shown in Fig. 5.19.

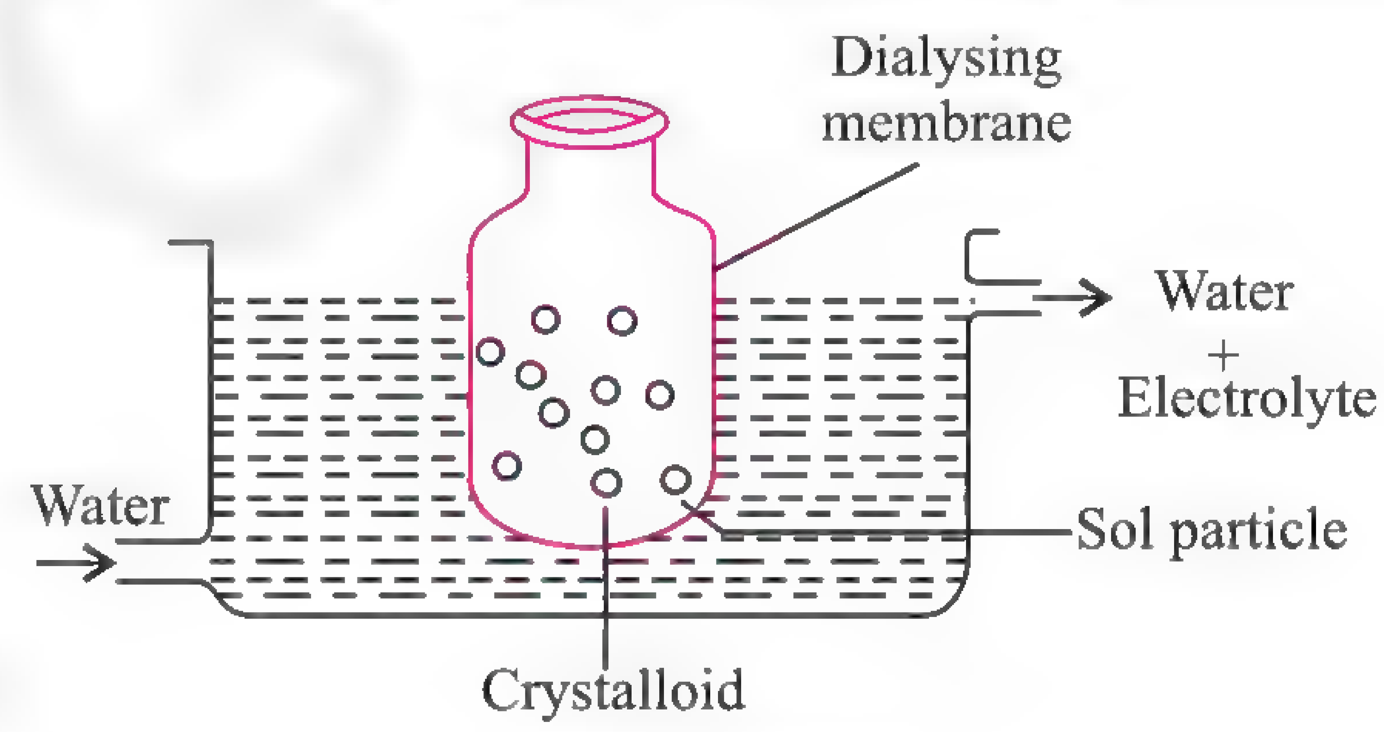


Fig. 5.19 Dialysis

In humans, kidneys perform dialysis in order to purify blood which is of colloidal nature. The most important application of dialysis process is the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work.

b. **Electro-dialysis:** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 5.20. the ions present in the colloidal solution migrate out to the oppositely charged electrodes.

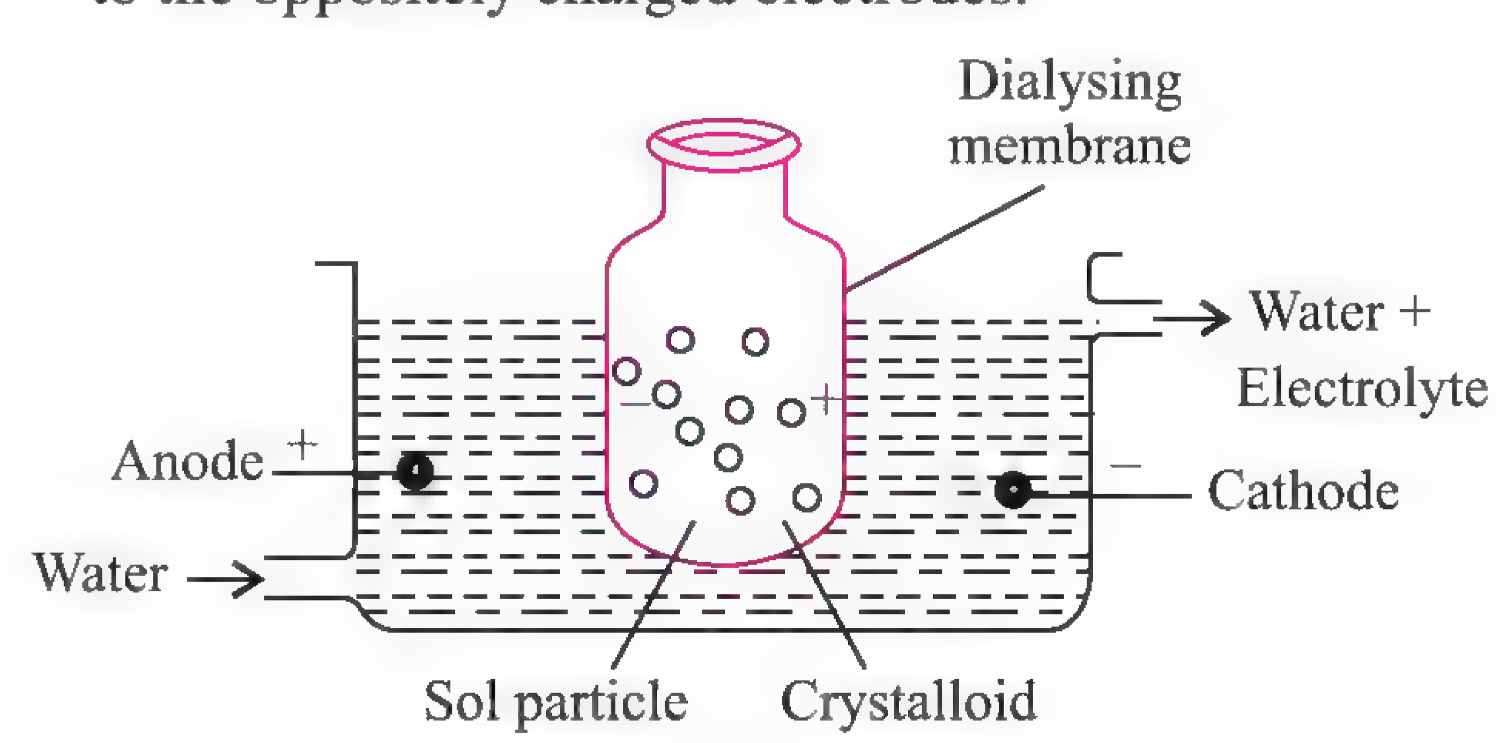


Fig. 5.20 Electrodialysis

c. **Ultrafiltration:** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes

present in the colloidal solution by specially prepared filters which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with *colloidion* solution to stop the flow of colloidal particles. The usual colloidion is a 4% solution of nitrocellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution, hardening formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from the rest of materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

d. **Ultracentrifugation:** In this method, the colloidal solution is placed in a high-speed ultracentrifuge. On centrifuging the colloidal particles settle down. The impurities remain in the dispersion medium and are removed by decantation. The settled colloidal particles are shaken with water containing peptizing agent to form the colloidal solution again.

5.5.4 Properties of Colloidal Solutions

The characteristic properties of colloidal solutions are as given below.

Physical Properties

a. **Heterogeneous nature:** A colloidal solution is heterogeneous in nature. It consists of two phases namely, the dispersed phase and the dispersion medium.

b. **Visibility:** Colloidal particles are too small to be seen with naked eye, but they become visible as bright spots against dark background when viewed through an ultra microscope due to scattering of light caused by them.

c. **Filterability:** The size of solute particles is smaller than the pore size of filter paper, and therefore, they can readily pass through a filter paper. Colloidal particles, however, cannot pass through ultra filters, parchment paper, or animal membrane.

d. **Surface tension and viscosity:** The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.

e. **Colligative properties:** A colloidal solution has very small value of mole fraction of dispersed phase due to high average molecular mass of the colloidal particles. As a result of all the colligative properties, colloidal solutions have quite low values when compared to true solutions, having same concentration. However, the low osmotic pressure of a colloidal solution is measurable and can be used to determine the molecular weight of colloidal particles.

Mechanical Properties

a. **Brownian movement:** The colloidal particles of a colloidal solution when viewed through an ultramicroscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and is known as Brownian movement (Fig. 5.21). This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The motion becomes intense at higher temperature.

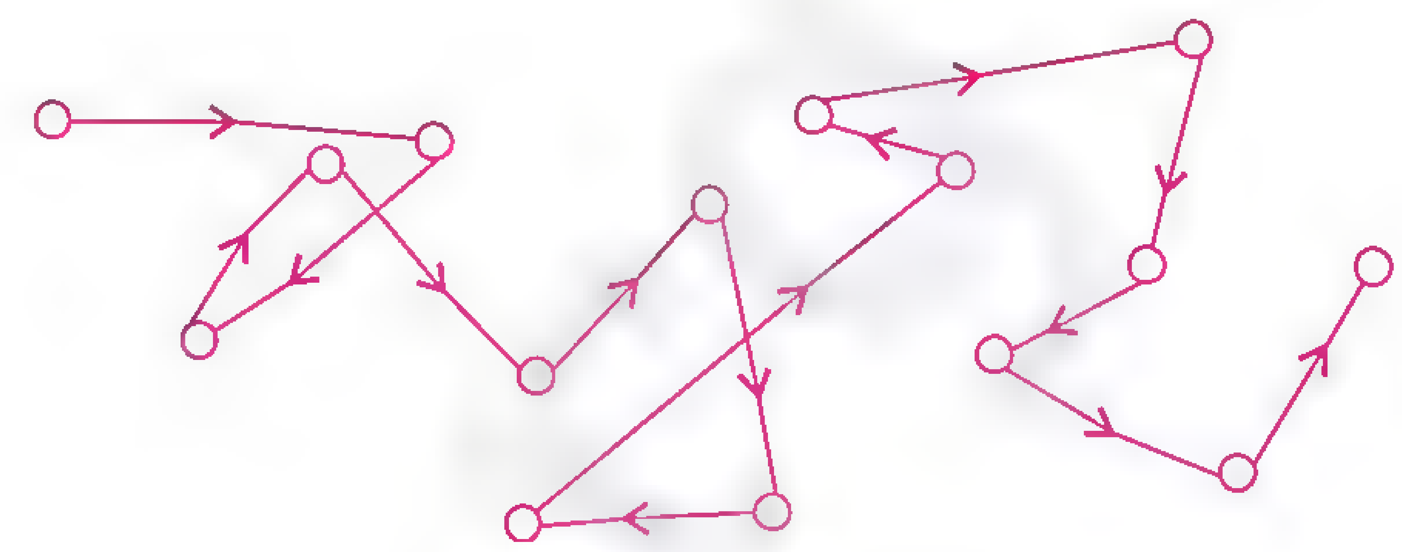


Fig. 5.21 Brownian movement

Cause of Brownian movement

The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. As the size of the particles increases, the probability of uneven bombardment decreases and the Brownian movement becomes slow. The Brownian movement has a stirring effect which does not permit the particles to settle and, thus, is responsible for the stability of sols.

Importance of Brownian movement

i. Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.

ii. It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.

b. **Diffusion:** colloidal particles such as solute particles of true solution diffuse from a region of higher concentration that of lower concentration. However, colloidal particles diffuse at a slower rate due to their large size and high molecular mass.

c. **Sedimentation:** The colloidal particles tend to settle down very slowly under the influence of gravity. The sedimentation or the rate of settling down can be increased by ultracentrifuge.

Optical Properties: Tyndall Effect

The scattering of light by the colloidal particles in a colloidal solution is known as Tyndall effect as it was first observed by Faraday and later studied in detail by Tyndall. Tyndall effect is caused by the scattering of blue part of light by the colloidal particles.

If a strong beam of light is passed through a colloidal solution placed in dark place, the path of the beam gets illuminated. The illuminated path of beam is called Tyndall cone (Fig. 5.22).

The scattering is caused if the size of particles is of the order of wavelength of light. The same effect is not observed when the light is passed through a true solution as the size of solution particles is too small to cause any scattering.

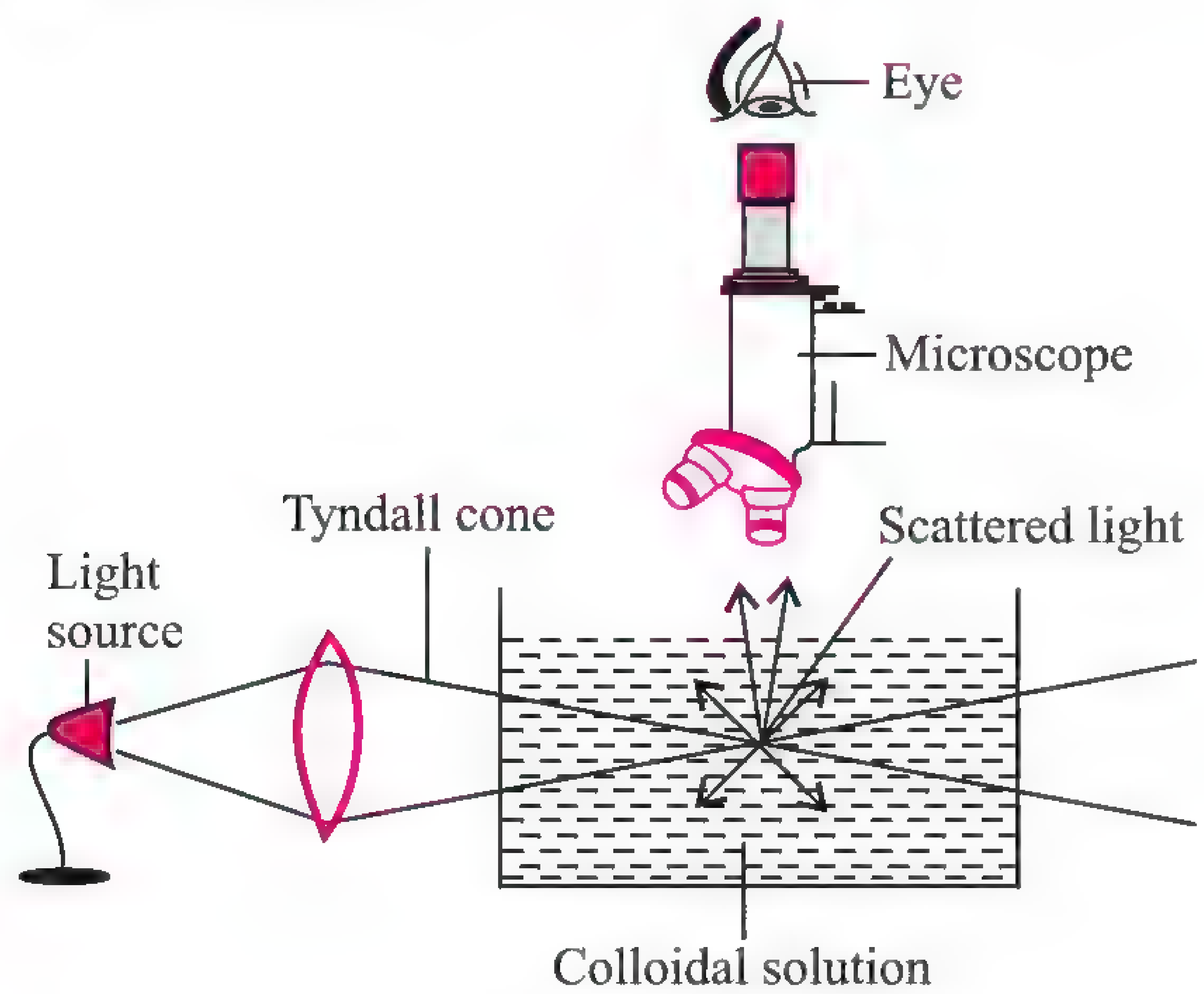


Fig. 5.22 Tyndall effect

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

a. The diameter of the dispersed particles is not much smaller than the wavelength of the light used.

b. The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.

Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

c. The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue, and finally golden.

Electric Properties

The colloidal particles always carry an electrical charge. The nature of this charge is same on all the particles in a given colloidal solution and may be either positive or negative. The presence of charge is responsible for the stability of these solutions. It may be noted that only the sol particles carry some charge while the dispersion medium has no charge.

A list of some common sols with the nature of charge on there particles is given below:

Positively charged sols	Negatively charged sols
• Hydrated metallic oxides, e.g., $Al_2O_3{\cdot}xH_2O$, $CrO_3{\cdot}xH_2O$, and $Fe_2O_3{\cdot}xH_2O$	• Metals, e.g., copper, silver, gold sols
• Basic dye stuffs, e.g., methylene blue sol Haemoglobin (blood)	• Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols Acid dye stuffs, e.g., eosin, congo red sols
• Oxides, e.g., TiO_2 sol	• Sols of starch, gum, gelatin, clay, charcoal, etc.

Origin of charges: The charges on the sol particles is due to various reason. Some of these are as follows:

a. Due to frictional electrification: The mutual rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.

b. Due to dissociation of surfactants: For example, dissociation of soap (sodium palmitate) results into ions as:

$$C_{15}H_{31}COONa \rightleftharpoons C_{15}H_{31}COO^{\ominus} + Na^{\oplus}$$

The cation ($Na^{\oplus}$) pass into solution while anion ($C_{15}H_{31}COO^{\ominus}$) aggregates due to weak attractive forces present in the hydrocarbon chains.

c. Due to preferential adsorption of ions from solution or due to formation of electrical double layer: Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in a dispersion medium, preferential adsorption of a ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

i. When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to $AgNO_3$ solution, positively charged sol results due to the adsorption of $Ag^{\oplus}$ ions from dispersion medium.

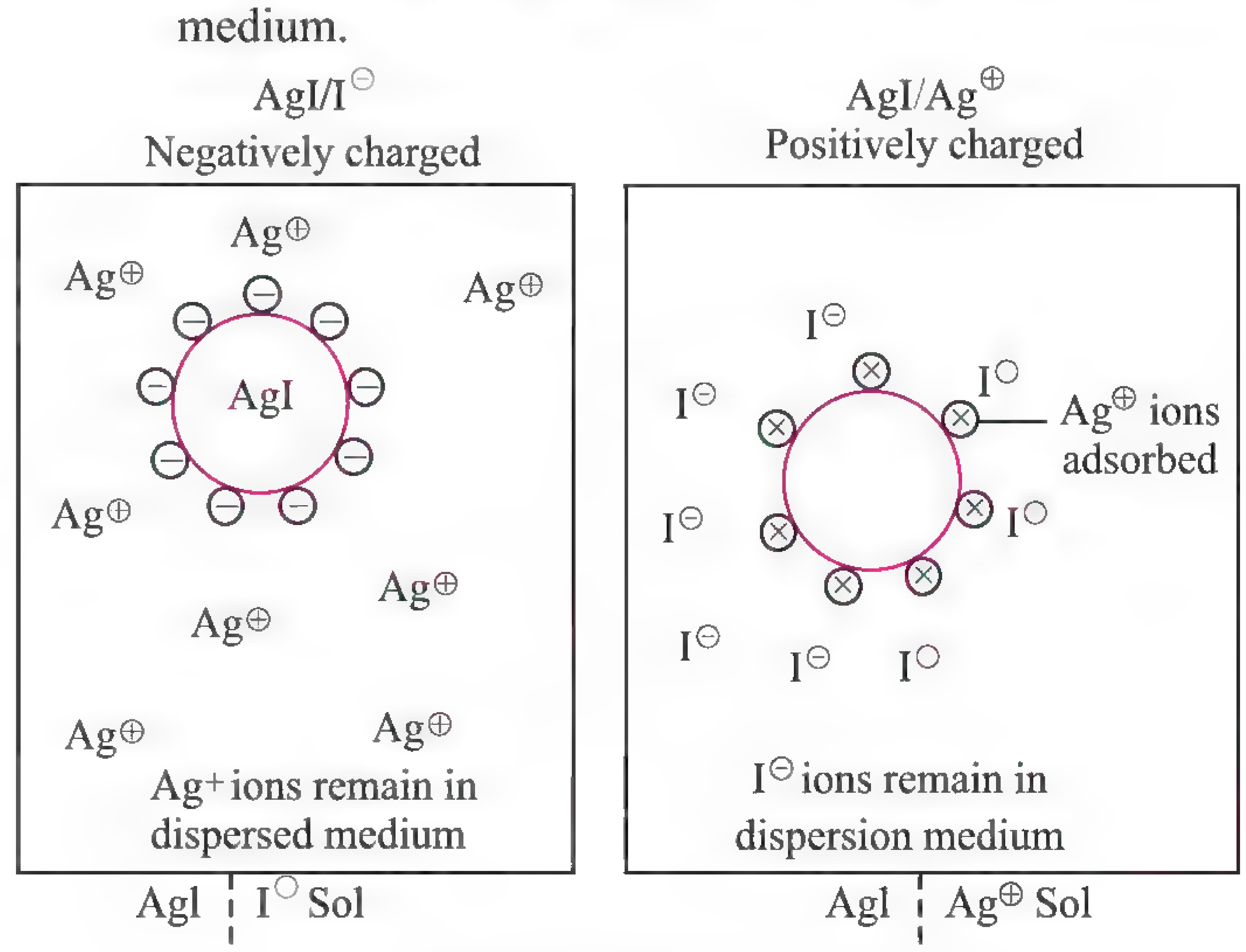


Fig. 5.23 Selective adsorption of ions

ii. If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to the adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of $OH^{\ominus}$ ions.

$Fe_2O_3{\cdot}xH_2O/Fe^{3+}$ Positively charged $\qquad$ $Fe_2O_3{\cdot}xH_2O/OH^{\ominus}$ Negatively charged

Electrokinetic potential or zeta potential

After acquiring a positive or a negative charge by selective adsorption on the surface of a colloidal particle, this layer attracts counter ions from the medium forming a second layer, as shown in Fig. 5.24.

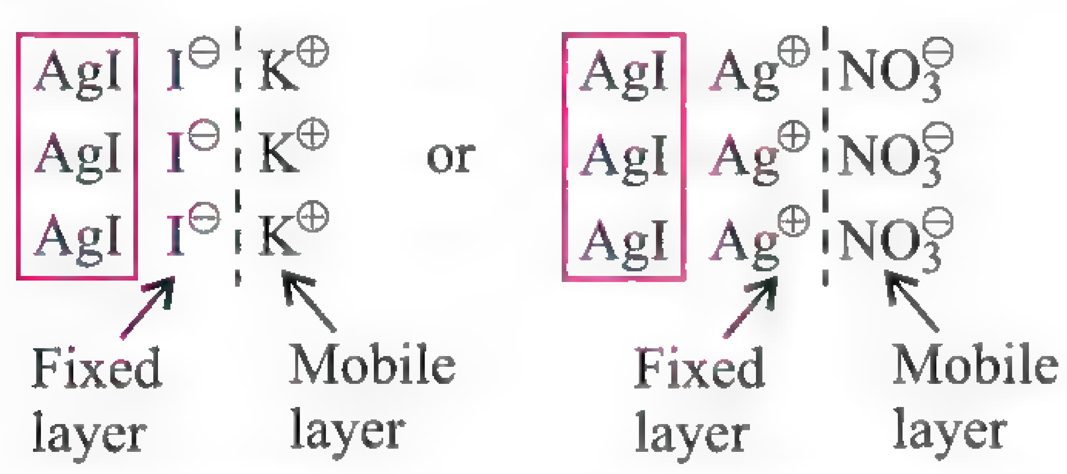


Fig 5.24 Formation of electric double layer

The combination of two layers of opposite charges around a colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer result in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the *electrokinetic potential* or *zeta potential*.

The presence of equal and similar charges on colloidal particles is largely responsible in providing to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

The electrical properties of colloidal solutions are related with two phenomena:

i. Electrophoresis
ii. Electro-osmosis

i. Electrophoresis: The existence of charge on colloidal particles is determined by electrophoresis experiment. In this experiment when electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards positive or negative electrodes depending upon their charge under the influence of electric field.

The phenomenon of the movement of colloidal particles under an applied electric field is called *electrophoresis*. The positive charged particles move towards the cathode while negatively charged particles move towards the anode. Thus, by observing the direction of movement of the colloidal particles, the sign of the charged carried by the particles can be determined.

These can be demonstrated by the following experimental setup (Fig. 5.25).

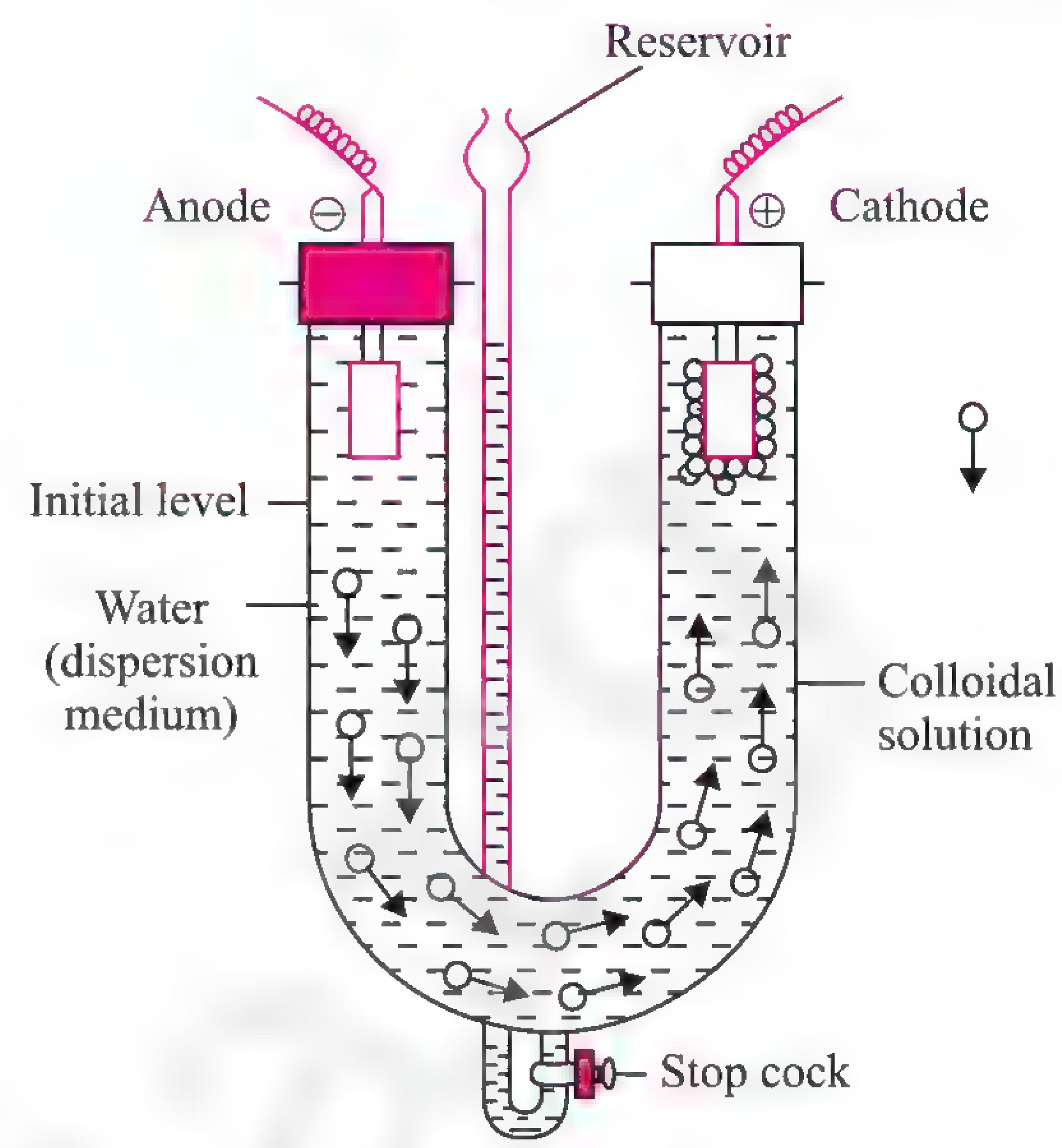


Fig. 5.25 Electrophoresis setup

ii. Electro-osmosis: Electro-osmosis may be defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move.

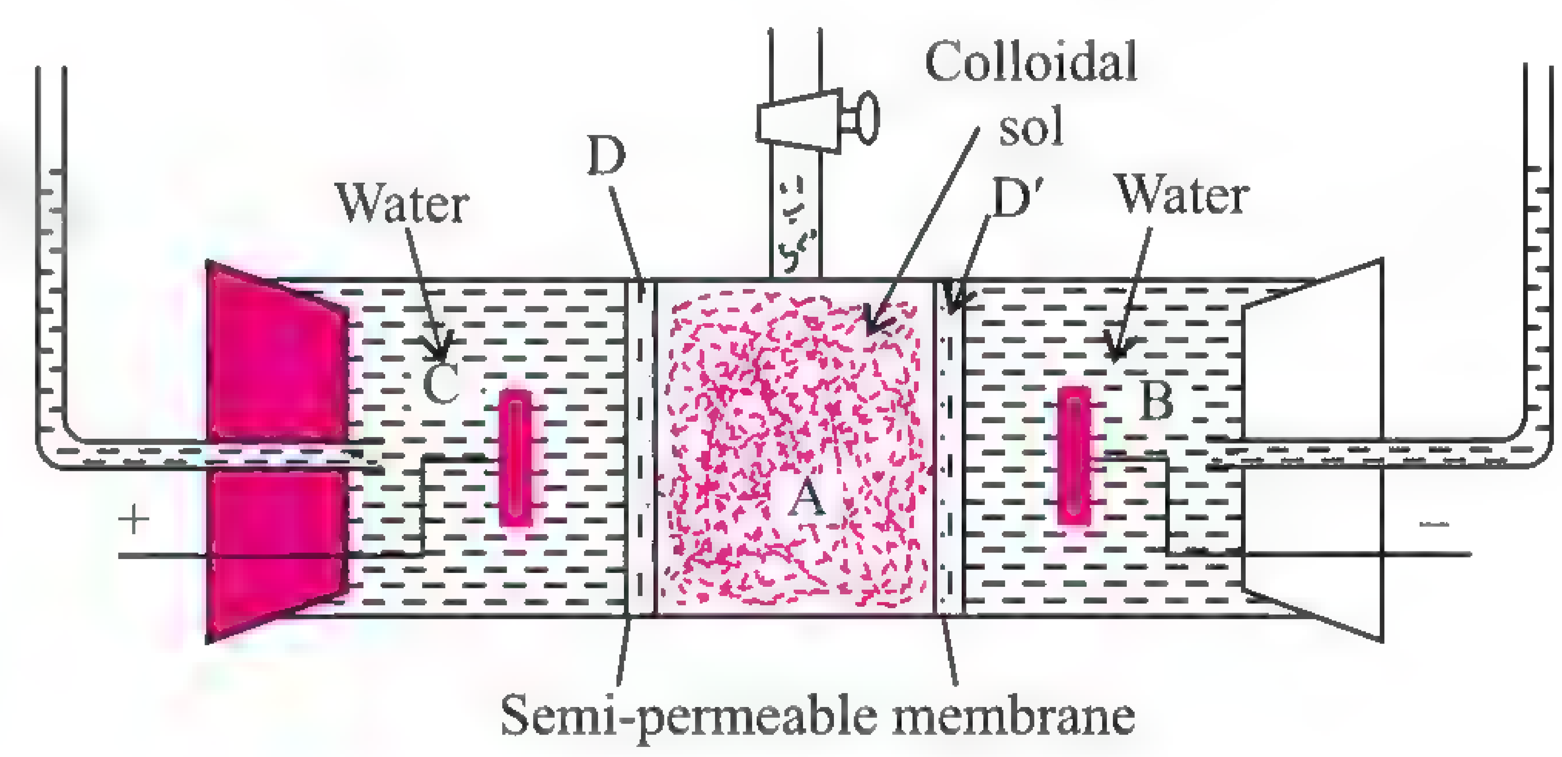


Fig. 5.26 Electro-osmosis

The electro-osmosis can be observed by a simple apparatus as shown in Fig. 5.26. The colloidal solution is placed in a compartment A separated from compartments B and C by semi-permeable membranes D and D′. The compartments B and C are filled with water up to the marks indicated by the side arms. When a potential is applied across the two electrodes placed near the membranes in B and C, the liquid level is observed to fall on one side and rise on the other side due to the passage of water through membranes D and D′. The direction of the flow of water depends on the charge of the colloid. For positively charged sols, the medium is negatively charged, and hence the flow will take place from C to B. On the other hand, for negatively charged sols, the reverse will occur and the level on the C side will rise.

5.5.5 Coagulation or Precipitation or Flocculation of Colloids

The stability of lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates

(or coagulate) and settle down under the force of gravity. *The process of settling of colloidal particles is called coagulation or. precipitation of the sol.* The coagulation of the lyophobic sols can be carried out in the following ways:

a. **By electrophoresis:** The colloidal particles move towards oppositely charged electrodes and get discharged and precipitated.
b. **By mixing two oppositely charged sols:** Oppositely charged sols when mixed in almost equal proportions, neutralize their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) brings them in the precipitated forms. This type of coagulation is called *mutual coagulation*.
c. **By boiling:** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.
d. **By persistent dialysis:** On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
e. **By addition of electrolytes:** When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralization leading to their coagulation. The ion responsible for the neutralization of charge on the particles is called the *coagulating ion*. A negative ion causes the precipitation of positively charged sol and vice versa.

Hardy Schulze Rule

The coagulation capacity of different electrolytes is different. It depends upon the valency of the *active ion* or called *flocculating ion* which is an ion-carrying charge opposite to the charge on the colloidal particles. According to Hardy Schulze rule, *greater the valency of the active ion or flocculating ion, greater will be its coagulating power.* Thus, according to Hardy Schulze rule:

a. The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
b. *The coagulating power of an electrolyte is directly proportional to the fourth power of the valency of the active ions (ions causing coagulation).* Greater is the valency of the oppositely charged ion of the electrolyte being added, faster is the coagulation. For example, to coagulate *negative sol of As_2S_3*, the coagulating power of different cations has been found to decrease in the order as:

$$Al^{3+} > Mg^{2+} > Na^{\oplus}$$

Similarly, to coagulate a *positive sol such as $Fe(OH)_3$*, the coagulating power of different anions has been found to decrease in the order.

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{\ominus}$$

The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as *coagulation value or flocculation value*. It is usually expressed as millimoles per litre. For example, the flocculating values (in millimoles per litre) for the coagulation of positively charged $Fe(OH)_3$ sol and negatively charged As_2S_3 sol are given in Table 5.10.

Table 5.10 Flocculating values (in millimole/litre) of common electrolytes

Electrolyte	Active ion (anion)	Flocculating value (millimole per litre)
Ferric hydroxide (+) sol		
KCl	$Cl^{\ominus}$	103
KBr	$Br^{\ominus}$	138
K_2SO_4	SO_4^{2-}	0.210
$Na_2C_2O_4$	$C_2O_4^{2-}$	0.238
$K_3[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$	0.096
Arsenic sulphide (+) sol		
NaCl	$Na^{\oplus}$	51
KCl	$K^{\oplus}$	50
$MgSO_4$	Mg^{2+}	0.72
$BaCl_2$	Ba^{2+}	0.69
$AlCl_3$	Al^{3+}	0.093

Table 5.10 shows that the coagulating power is inversely proportional to coagulation value or flocculation value.

The relative coagulating powers may be compared as:

$$\frac{\text{Coagulating power of electrolyte 1}}{\text{Coagulating power of electrolyte 2}} = \frac{\text{Coagulating value of electrolyte 2}}{\text{Coagulating value of electrolyte 1}}$$

For example, for coagulation of negatively charged As_3S_3 sol

$$\frac{\text{Coagulating power of } AlCl_3}{\text{Coagulating power of NaCl}} = \frac{\text{Coagulating value of NaCl}}{\text{Coagulating value of } AlCl_3} = \frac{51}{0.093} = 548$$

Thus, $AlCl_3$ has 548 times more coagulating power than NaCl.

Illustration 5.39

For the coagulation of 10 mL of $Fe(OH)_3$ sol, 2 mL of 1 M KBr is required. What is the flocculation value of KBr?

Sol. 2 mL of 1 MKBr contains KBr $= \frac{1}{1000} \times 2$ mol $= 2$ mmol

Thus, 10 mL of $Fe(OH)_3$ sol requires KBr for complete coagulation = 2 mmol

∴ 1 L, i.e., 1000 mL, of the sol requires KBr for complete coagulation = 200 mmol

Hence, flocculation value of KBr = 200

Coagulation of lyophilic sols

There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (a) by adding an electrolyte and (b) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

5.5.6 Protection of Colloids

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and, thus, protect the latter from electrolytes. Lyophilic colloids used for this purpose are called *protective colloids*.

Gold number: The lyophilic colloids differ in their protective power. The protective power is measured in terms of *gold number* and is defined as the *number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% sodium chloride solution.*

The gold number of a few protective colloids is as follows:

S. No.	Protective colloid	Gold number
1.	Gelatin	0.005–0.01
2.	Haemoglobin	0.03
3.	Gum arabic	0.15
4.	Egg albumin	0.08–0.10
5.	Potato starch	25
6.	Sodium oleate	0.4
7.	Gum tragacanth	2
8.	Starch	25–50

It may be noted that smaller the value of the gold number, greater will be the protecting power of protective colloids.

Therefore, the reciprocal of gold number is a measure of the protective power of the colloid. Thus, out of the list given above, gelatin is the best protective colloid.

Congo rubin number: The protective action of a lyophilic colloid is sometimes expressed in terms of congo rubin number, as suggested by Ostwald. It is defined as the minimum amount of the protective colloid in milligrams that prevent the colour change of 100 mL of 0.01% congo rubin dye to which 0.16 g equivalent of KCl is added.

ILLUSTRATION 5.40

On addition of 1 mL solution of 10% NaCl to 10 mL gold sol in the presence of 0.0250 g of starch, the coagulation is just prevented. What is the gold number of starch?

Sol. Amount of starch in mg that prevent coagulation by 1 mL of 10% NaCl solution = $0.025 \times 1000 = 25$.

Hence, gold number = 25.

5.5.7 Colloids Around Us

Most of the substances we come across in our daily life are colloids. The meals we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

Following are the interesting and noteworthy examples of colloids:

a. **Blue colour of the sky:** Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

b. **Fog, mist, and rain:** When a large mass of air containing dust particles is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet.

   It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

c. **Food articles:** Milk, butter, halwa, ice-creams, fruit juices, etc., are all colloids in one form or the other.

d. **Blood:** It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

e. **Soils:** Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

f. **Formation of delta:** River water contains charged colloidal particles of clay, sand, and many other materials. Sea water is a very big store house of a variety of electrolytes dissolved in it. As soon as river water comes in contact with sea water, the electrolytes present in sea water coagulate the suspended colloidal particles which ultimately settle down at the point of contact. Thus, the level of the river bed rises. As a result, water adopts a different course and delta is formed in due course of time (Fig. 5.27).

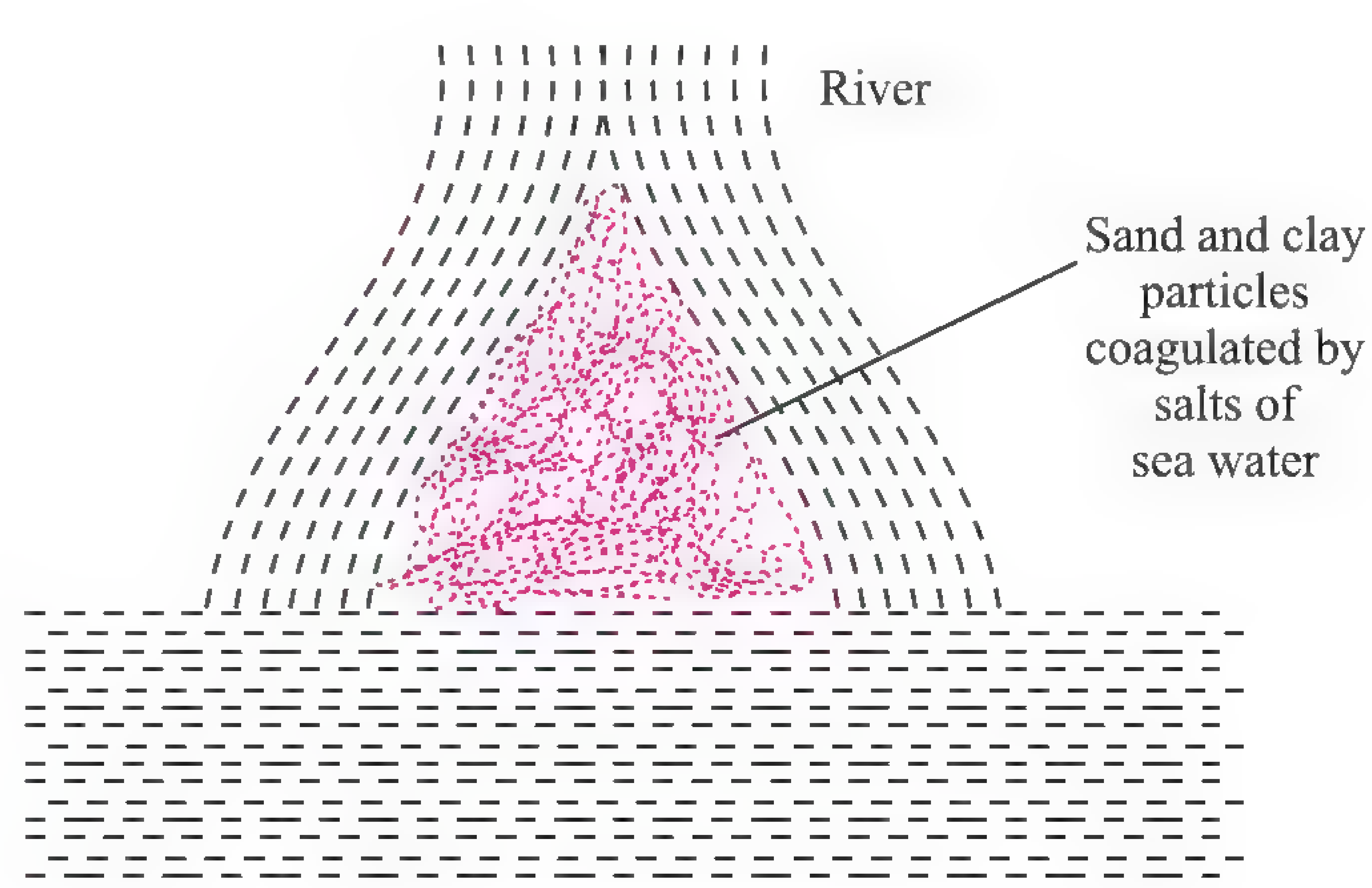


Fig. 5.27 Formation of delta

5.5.8 Applications of Colloids

Colloids are widely used in the industry. Following are some examples:

a. **Electrical precipitation of smoke:** Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator (Fig. 5.28).

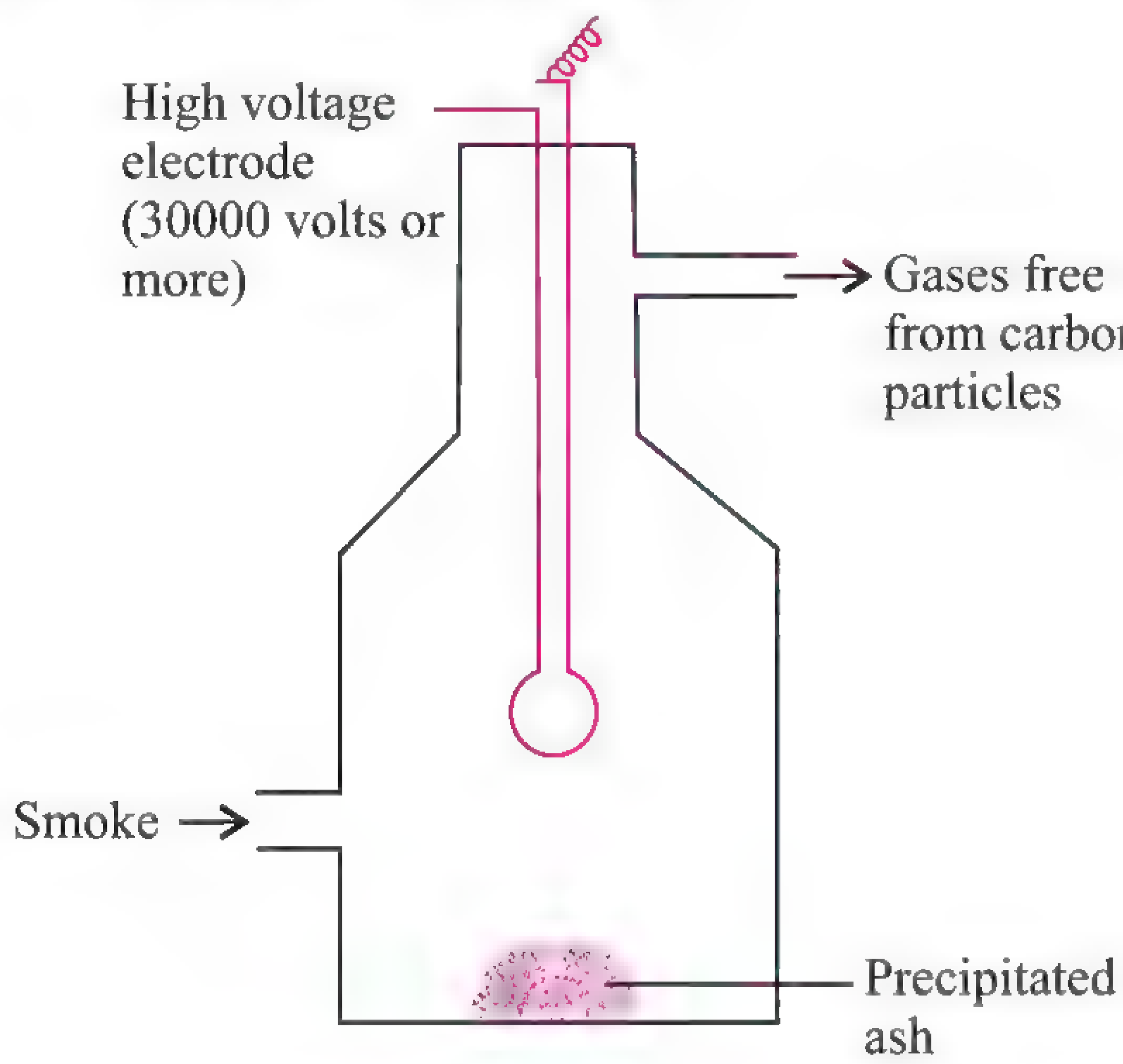


Fig. 5.28 Cottrell smoke precipitator

b. **Purification of drinking water:** The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

c. **Medicines:** Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kala azar. Colloidal gold is used for intramuscular injection. Milk of magnesia an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.

d. **Tanning:** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

e. Cleansing action of soaps and detergents

f. **Photographic plates and films:** Photographic plates or films are prepared by coating an emulsion of the light- sensitive silver bromide in gelatin over glass plates or celluloid films.

g. **Rubber industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

h. **Industrial products:** Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions.

5.6 EMULSIONS

Emulsions are colloidal solutions in which both the dispersed phase and dispersion medium are liquids. It can be defined as the dispersion of finely divided droplets in another liquid. Any two immiscible liquids can form an emulsion. For example, milk is a naturally occurring emulsion in which the particles (or globules) of liquid fats are dispersed in water.

Emulsions are generally prepared by vigorously shaking two immiscible or partially miscible liquids, through a colloid mill, called the homogenizer. Generally, one of the two liquids is water.

5.6.1 Types of Emulsions

Emulsions are mainly of two types:

a. **Oil-in-water-type emulsions (O/W type):** In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. For example, milk, vanishing cream, etc.

b. **Water-in-oil-type emulsions (W/O type):** In this type of emulsion, water is the dispersed phase and oil is the dispersion medium. For example, butter, cod liver oil, cold cream, etc.

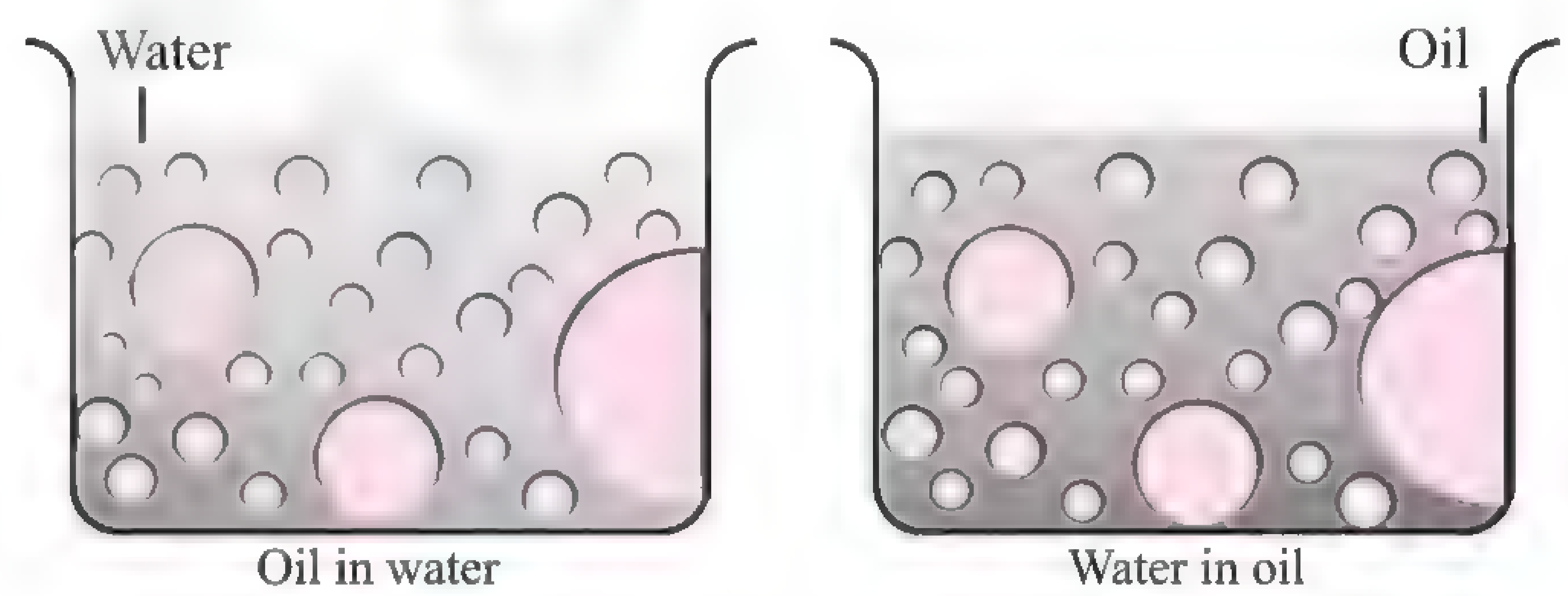


Fig. 5.29 Types of emulsions

Emulsions of oil and water are unstable and sometimes on standing they separate into two layers. For the stabilization of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agents form an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lamp black, etc.

Role of an Emulsifier

The stabilization of an emulsion by means of emulsifier is called *emulsification*.

The main function of the emulsifier is to reduce the interfacial tension between the two liquids forming the emulsion. Emulsifiers are generally long-chain molecules having polar groups.

The role of an emulsifier can be explained by taking the example of soap as an emulsifier. As already studied, the soaps are sodium or potassium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}COONa$), sodium stearate ($C_{17}H_{35}COONa$). A molecule of soap consists of two parts: hydrocarbon non-polar part (e.g., $C_{15}H_{31}$, $C_{17}H_{35}$, etc.) which is soluble in oil and the polar group ($—COO^{\ominus}Na^{\oplus}$) which is soluble in water.

$$R—COO^{\ominus}Na^{\oplus}$$

When a drop of oil is surrounded by soap solution, R-part of the soap remains in oil and the $COO^{\ominus}Na^{\oplus}$ part remains in water as shown in Fig. 5.30. As a result, soap molecules get concentrated over the surface of the drop of oil and, therefore, form protective film around each oil drop. As a result, the interfacial tension

between oil and water decreases, and therefore, they are intermixed to form the emulsion.

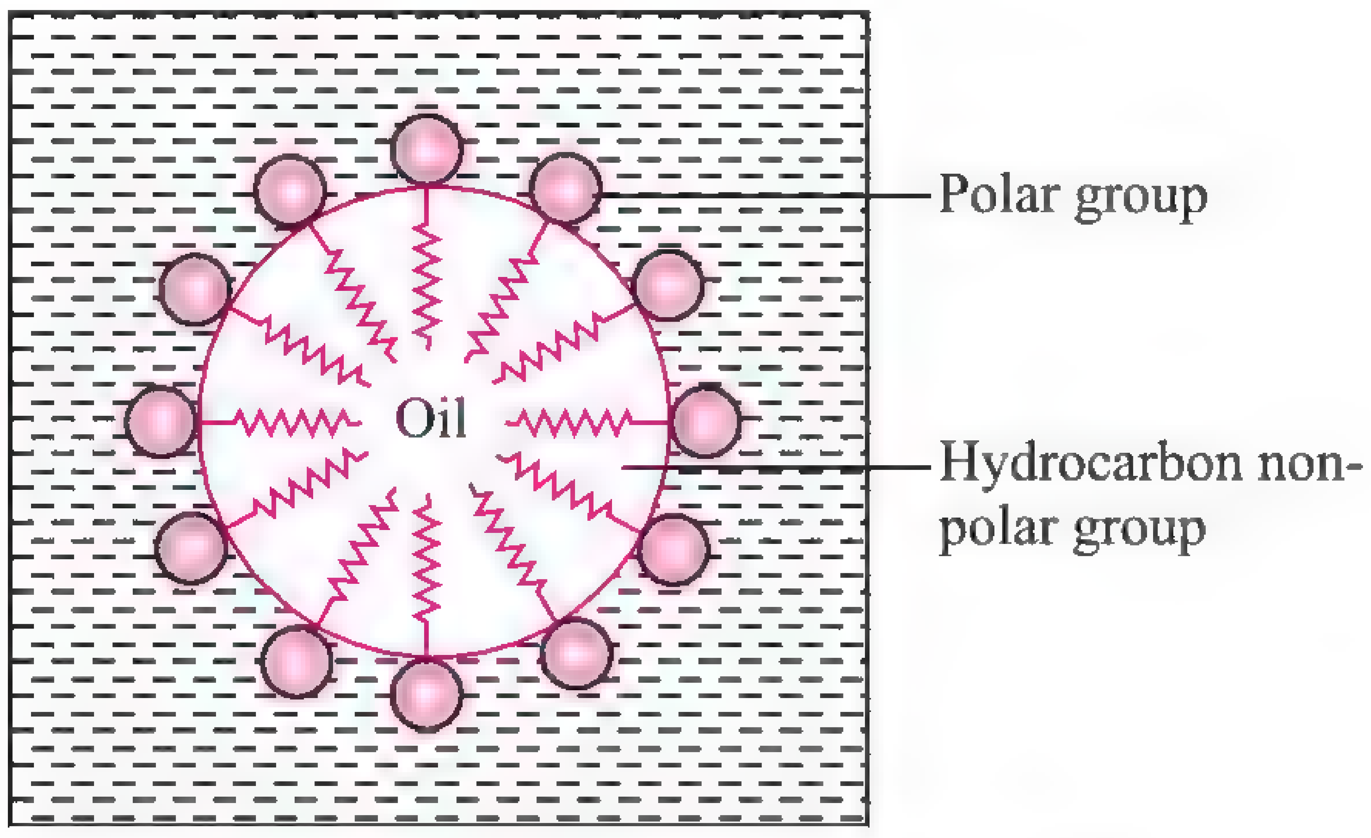


Fig 5.30 Role of soap as an emulsifier

Emulsions can be diluted with any amount of the dispersion medium On the other hand, the dispersed liquid when mixed forms a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

5.6.2 Identification of Emulsions

The oil-in-water and water-in-oil emulsions can be identified by the following tests:

a. **Microscopic method:** To a small amount of the given emulsion, a few drops of water are added. The water will mix completely if the emulsion is of oil-in-water type. Likewise, for the water-in-oil emulsion the miscibility with a few drops of oil can be tested. The miscibility can be seen under a microscope.

b. **Conductance method:** This method is based upon adding a small amount of an electrolyte to the emulsion. If the conductance increases, the emulsion is oil-in-water type and if there is no significant change, it is water-in-oil type.

c. **Dye method:** A small amount of oil-soluble dye is added to the emulsion. If it is water-in-oil type, it becomes deeply coloured, otherwise it remains colourless.

5.6.3 Properties of Emulsions

Following are the characteristic properties of emulsions:

a. Emulsions exhibit all the properties such as Tyndall effect, Brownian movement, electrophoresis, coagulation on the addition of electrolytes (containing multivalent positive ions, as the dispersed particles, i.e., globules are usually negatively charged) as shown by colloidal sols.

b. The size of the dispersed particles in an emulsion is larger than those in the sols. It ranges from 100 Å to 10000 Å.

c. Emulsions can be broken to yield the constituent liquid by heating, centrifuging, by adding larger amounts of the electrolytes to precipitate out the dispersed phase, or by chemical destruction of the emulsifying agent. The separation of cream from milk is a well-known example of centrifuging.

The process of breaking an emulsion to yield the constituent liquids is called *demulsification.*

5.6.4 Application of Emulsions

Emulsions are useful in a number of way. A few of the applications are given below.

a. In the metallurgical processes, the concentration of ore by froth floatation process is based upon the treatment of the powdered ore with oil emulsion. The valuable particles of the ore form foam which comes to the surface and is skimmed off.

b. Asphalt emulsified in water is used for building roads without the necessity of melting the asphalt.

c. Milk which is an important constituent of our diet is an emulsion of liquid fats in water.

d. Several oily drugs are prepared in the form of emulsions.

e. The cleansing action of ordinary soap for washing clothes, crockery, etc., is based upon the formation of oil-in-water emulsion.

f. The digestion of fats in the intestine takes place by the process of emulsification. A small amount of the fat reacts with the alkaline solution present in the intestine to form a sodium soap. This soap causes the emulsification of the rest of the fat thereby making the function of the digestive enzymes easier in carrying out the metabolic processes.

5.6.5 Harmful Effects of Emulsions

The formation of emulsions is sometimes harmful. For example, petroleum forms emulsion with water. Thus, in the petroleum wells, we get an emulsion sometimes instead of petroleum alone. Likewise, in the area where small amounts of petroleum are present, the well water becomes unfit for use.

5.7 GELS

A gel is a colloidal system in which a liquid is dispersed in a solid. Under certain conditions, the lyophilic sols may be coagulated to give a semi-solid jelly-like mass which encloses all the liquid present in the sol. The process of gel formation is called *gelation* and the colloidal system formed is called *gel*. The common examples of gel are: gum arabic, gelatin, processed cheese, silicic acid, ferric hydroxide, etc.

Gels are formed by the interlocking of the particles of solid dispersion medium in the form of a loose framework inside which liquid (dispersed phase) is contained.

When the gel is allowed to stand for a long time, it *shrinks* and loses the entire liquid held by it. This shrinking of gel is termed as *syneresis* or *weeping*.

Gels may be classified into two types:

a. Elastic gels

b. Non-elastic gels

The main points of difference between the two are as follows:

Elastic gels	Non-elastic gels
a. Gels which possess the property of elasticity, i.e., they change to dehydratic solid mass which can again be converted into gel by addition of water followed by heating and cooling.	**a.** Gels which do not possess the property of elasticity, i.e., they change into solid mass on dehydration which becomes rigid and cannot be converted into the original form by heating with water.
b. When placed in contact with water they absorb water and swell. This property is called imbibition.	**b.** They do not show the phenomenon of imbibition.
c. Examples include gelatin, agar-agar, starch, etc.	**c.** Most common example is silicic acid.

Thixotropy: Some gels, such as gelatin, on mechanical shaking lose their semi-solid gel-like character and change into a liquid sol. This sol on standing again changes into gel. This phenomenon is known as *thixotropy*.

5.7.1 Lyotropic Series or Hofmeister Series

When a gel is placed in a suitable liquid, it absorbs a large volume of the liquid. The phenomenon is called *imbibition* or *swelling*. The effect of the presence of salts on swelling was studied by Hofmeister (1891). He found that for the salts of the same cation (e.g. $Na^{\oplus}$) the effect of certain other anions was to inhibit the imbibition while that of certain other anions was to favour the imbibition. For example in case of iodides, the swelling is so high that the gel disperses into sol even at room temperature. In other cases, the sol is formed by warming the swollen gel. The order of the temperature to which the gel must be heated in the presence of various anions, before it changes into sol in called *Hofmeister series* or *lyotropic series*. The order is:

$\text{Citrate}^{3-} > \text{Tartarate}^{2-} > SO_4^{2-} > PO_4^{3-} > \text{Acetate} > Cl^{\ominus} > NO_3^{\ominus} > Br^{\ominus} > I^{\ominus} > CNS^{\ominus}$.

The anions from citrate to acetate inhibit the imbibition while from $Cl^{\ominus}$ to $CNS^{\ominus}$ favour the imbibition.

Illustration 5.41

What are micelles? How do they differ from ordinary colloidal particles? Give two examples of micelles-forming substances.

Sol. There are some substances which at low concentration behave as normal electrolyte but at higher concentrations exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles.

The formation of micelles takes place only above a particular temperature called Kraft temperature and above a particular concentration called critical micellization concentration (CMC). On dilution these colloids revert back to individual ions.

Examples are soaps and synthetic detergents.

Illustration 5.42

State Hardy Schulze rule.

Sol. Greater the valency of the action ion of the electrolyte, greater will be its precipitating action.

$Al^{3+} > Mg^{2+} > Na^{\oplus}$ for negatively charged sols

$PO_4^{3-} > SO_4^{2-} > Cl^{\ominus}$ for positively charged sols

Illustration 5.43

Describe the following types of colloids, giving an example for each:

a. Multimolecular colloids

b. Macromolecular colloids

Sol.

a. Multimolecular colloids: A large number of atoms or smaller molecules of a substance on dissolution aggregate together to form species having size (diameter < 1 nm) in the colloidal range (1–1000 nm). Such species are, known as multimolecular colloids. For example, a sulphur sol consist of particles containing a thousand or more S_8 sulphur molecules.

b. Macromolecular colloids: Macromolecules (starch, cellulose, proteins and nylon, polyethene, etc.) when dissolved in suitable solvent form a solution wherein the size of the macromolecule may fall within the colloidal range. Such systems are called macromolecular colloids.

Illustration 5.44

What is Kraft temperature?

Sol. Kraft temperature is the minimum temperature above which the formation of miscelles takes place.

Illustration 5.45

What is meant by the term peptization?

Sol. The process of conversion of a freshly prepared precipitate into a colloidal solution by adding a suitable electrolyte is called peptization.

Illustration 5.46

Which one of the following electrolytes is most effective for the coagulation of $Fe(OH)_3$ sol and why?

$$NaCl,\ Na_2SO_4,\ Na_3PO_4$$

Sol. $Fe(OH)_3$ is a positively charged sol. According to Hardy Schulze rule, greater the charge on an oppositely charged ion of the electrolyte added, more effective it is in bringing about the coagulation. Hence, Na_3PO_4 (containing PO_4^{3-} ions) is most effective.

Illustration 5.47

How is dialysis carried out? Mention its one application.

Sol. Dialysis is used for purification of colloidal solution. It is carried out by putting impure colloidal solution in a parchment paper bag and then dipping it in distilled water. After some time, the molecules and ions diffuse through the membrane into the water leaving the pure colloidal solution behind. An important application of dialysis is during the purification of blood in the artificial kidney machine.

ILLUSTRATION 5.48

For the coagulation of 100 mL of arsenious sulphite sol, 5 mL of 1 M NaCl is required. What is the flocculation value of NaCl?

Sol. 5 mL of 1 M NaCl contains NaCl $= \frac{1}{1000} \times 5$ mol $= 5$ mmol

Thus, 100 mL of As_2S_3 sol require NaCl for complete coagulation = 5 mmol

$\therefore$ 1 L, i.e., 1000 mL of the sol requires NaCl for complete, coagulation = 50 mmol

Therefore, the flocculation value of NaCl = 50

ILLUSTRATION 5.49

The coagulation of 200 mL of a positive colloid took place when 0.73 g HCl was added to it without changing the volume much. The flocculation value of HCl for the colloid is

a. 36.5 **b.** 100 **c.** 200 **d.** 150

Sol.

b. 200 mL of the sol requires = 0.73 g HCl

Moles of HCl $= \frac{0.73}{36.5}$ mol $= 0.02$ mol $= 20.0$ mmol

Therefore, 1000 mL (1 L) of the sol will require

$$= \frac{20}{200} \times 1000 = 100 \text{ mmol}$$

ILLUSTRATION 5.50

What is observed when sodium chloride is added to a colloidal solution of ferric hydroxide?

Sol. When sodium chloride is added to ferric hydroxide solution, the solution gets coagulated. This is because $Cl^{\ominus}$ ions from NaCl neutralize the +ve charge on $Fe(OH)_3$ solution.

ILLUSTRATION 5.51

Give two examples of colloidal solutions of liquid dispersed in solid. What is the name of the colloidal solution?

Sol. Jelly, cheese. The name of these colloidal solutions is gel.

ILLUSTRATION 5.52

The coagulation of 100 mL of a colloidal Solution of gold is completely prevented by the addition of 0.30 g of starch to it before adding 1 mL of 10% NaCl solution. Find out the gold number of starch?

Sol. Starch added to 100 mL of gold sol to completely prevent coagulation by 1 mL of 10% NaCl sol = 0.30 g = 300 mg Starch required to be added to 10 mL of gold sol to completely prevent coagulation by 1 mL of 10% NaCl sol = 30 mg

Therefore, by definition, gold number of starch = 30

ILLUSTRATION 5.53

50 mL of standard gold solution needs 0.05 mg of gelatin for its protection from coagulation. Calculate the gold number of gelatine?

Sol. 50 mL of standard gold sol requires = 0.05 mg of gelatin Therefore, 10 mL of standard gold sol requires

$$= \frac{0.05}{50} \times 10 = 0.01 \text{ mg of gelatine}$$

$\therefore$ Gold number = 0.01

ILLUSTRATION 5.54

Explain the following observations:

a. Lyophilic colloid is more stable than lyophobic colloid.

b. Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.

c. Sky appears blue in colour.

Sol.

a. It is due to the greater force of attraction between dispersed phase and dispersion medium in lyophilic colloid than lyophobic colloid.

b. $Fe(OH)_3$ sol is positively charged which is coagulated by negatively charged $Cl^{\ominus}$ present in sodium chloride solution.

c. Sky appears blue in colour due to the scattering of light by colloidal particles. This is known as Tyndall effect.

ILLUSTRATION 5.55

What is the difference between a colloidal solution, gel, and emulsion?

Sol. In a colloidal sol, the dispersed phase is a solid and the dispersion medium is a liquid. In a gel, it is just the opposite. In an emulsion, both the dispersed phase and dispersion medium are liquids.

ILLUSTRATION 5.56

What type of colloidal sols are formed in the following:

a. Sulphur vapours are passed through cooled water.

b. White of an egg is mixed with water.

c. Soap solution.

Sol.

a. *Multimolecular* because sulphur molecules associate together to form colloidal sol.

b. *Macromolecular* because protein molecules present in the white of the egg are macromolecules soluble in water.

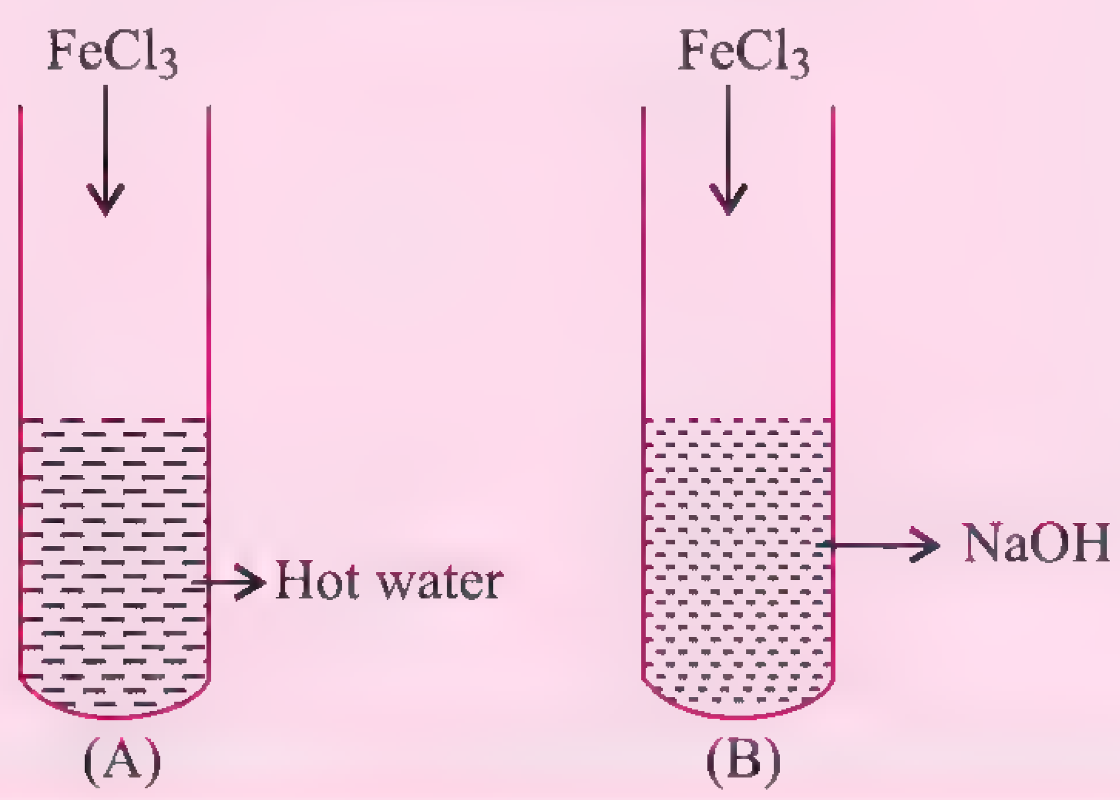
c. *Associated* because $RCOO^{\ominus}$ ions associate together to form micelles.

ILLUSTRATION 5.57

A colloidal solution of ferric oxide is prepared by two different methods as shown below.

a. What is the charge on colloidal particles in the two test tubes (A) and (B)?

b. Give reasons for the origin of charge.



Sol.

a. Colloidal particles of test tube (A) are positively charged where as colloidal particles of test tube (B) are negatively charged.

b. In test tube (A), Fe^{3+} is adsorbed on the precipitate $Fe_2O_3 \cdot xH_2O$ [or $Fe_2O_3 \cdot xH_2O/Fe^{3+}$ is formed].

In test tube (B), $\overset{\ominus}{O}H$ ion is adsorbed on the precipitate $Fe_2O_3 \cdot xH_2O$ [or $Fe_2O_3 \cdot xH_2O/\overset{\ominus}{O}H$ is formed].

ILLUSTRATION 5.58

Explain the following observations:

a. A beam of light passing through a colloidal solution has a visible path.

b. Passing an electric current through a colloidal solution removes colloidal particles from it.

c. Ferric hydroxide sol coagulates on addition of potassium sulphate.

Sol.

a. This is due to scattering of light by the colloidal particles (called Tyndall effect).

b. This is due to charge on the colloidal particles so that they migrate towards the oppositely charged electrode.

c. Ferric hydroxide is a positively charged sol and is coagulated by SO_4^{2-} ions produced by K_2SO_4.

ILLUSTRATION 5.59

Compare the coagulation power of $AlCl_3$ with that of NaCl. Given that their coagulation values are 0.093 and 52 respectively.

Sol. As coagulation power is inversely proportional to coagulation value, the ratio of their coagulation power will be

$$\frac{\text{Coagulation power of } AlCl_3}{\text{Coagulation power of NaCl}}$$

$$= \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of } AlCl_3} = \frac{52}{0.093} = 559$$

Thus, $AlCl_3$ has 559 times greater coagulation power than NaCl.

ILLUSTRATION 5.60

Compare the coagulating power of HCl with that of KBr. Given the coagulation values are 30.8 and 138, respectively?

Sol. The coagulation power is inversely proportional to the coagulation value, the ratio of their coagulation power is

$$\frac{\text{Coagulation power of HCl}}{\text{Coagulation power of KBr}}$$

$$= \frac{\text{Coagulation value of KBr}}{\text{Coagulation value of HCl}} = \frac{138}{30.8} = 4.48$$

Thus, HCl has 4.48 times greater coagulation power than KBr.

ILLUSTRATION 5.61

What modification can you suggest in the Hardy Schulze law?

Sol. According to the Hardy Schulze law, the coagulation ion has charge opposite to that on the colloidal particles. Hence, the charge on colloidal particles is neutralized and coagulation occurs. The law can be modified to include the following:

When oppositely charged sols are mixed in proper proportions to neutralize the charges of each other, coagulation of both the sols occurs.

ILLUSTRATION 5.62

Why is it essential to wash the precipitate with water before estimating it quantitatively?

Sol. Some amount of the electrolytes mixed to form the precipitate remain adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes (or any other impurities) before estimating it quantitatively.

ILLUSTRATION 5.63

What is meant by critical micellization concentration?

Sol. The micelle may be defined as the aggregated particles formed by associated colloids in solution. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC). Every micelle system has a specific value of CMC.

ILLUSTRATION 5.64

What type of substances form lyophobic sols?

Sol. Substances such as metals, their sulphides, etc., which do not mix directly with the dispersion medium form a lyophobic sol.

ILLUSTRATION 5.65

Define emulsification?

Sol. The process of making an emulsion from an oil is termed as emulsification.

ILLUSTRATION 5.66

Gelatin is generally added to ice creams. Why?

Sol. Ice cream is an emulsion of milk or cream in water, i.e., oil-in-water type. Gelatin is added to act as an emulsifier, i.e., it helps to stabilize the emulsion.

ILLUSTRATION 5.67

What is the significance of reciprocal of "gold number"?

Sol. Smaller the gold number, greater is its protective power. Hence, the reciprocal of gold number is a direct measure of the protective power of the colloid.

ILLUSTRATION 5.68

What is common in aqua sols and solid aerosols? How do they differ?

Sol. Aquasol and solid aerosol both have solid as the dispersed phase. They differ in dispersion medium. Aquasols have water as the dispersion medium, while aerosols have gas as the dispersion medium.

ILLUSTRATION 5.69

What is colloidion?

Sol. Colloidion is cellulose nitrate peptized by ethanol.

ILLUSTRATION 5.70

Define colloidal solution?

Sol. A colloidal solution is a state in which the particle size lies between 1 nm and 100 nm. It appears to be homogeneous but actually it is heterogeneous.

ILLUSTRATION 5.71

A sol of AgI can be positively or negatively charged. Explain how and why?

Sol. Charge on the colloidal particles is due to the preferential adsorption of common ions. AgI on shaking with excess of KI adsorbs negative $I^{\ominus}$ ions and hence is negatively charged. However, on shaking AgI with excess of $AgNO_3$ solution, it will adsorb $Ag^{\oplus}$ ions and hence becomes positively charged.

ILLUSTRATION 5.72

Give four uses of emulsion.

Sol.

a. The concentration of sulphide ore by froth flotation process is based on emulsification.

b. Phenyl, used as disinfectant, is an emulsion of oil in water.

c. Milk is an emulsion of fat in water.

d. Butter is an emulsion of water dispersed in fat

ILLUSTRATION 5.73

Give an example of an associated colloid?

Sol. Soaps and detergents are associated colloids.

ILLUSTRATION 5.74

Give one example of positively charged sol and one example of negatively charged sol.

Sol. $Fe(OH)_3$ is a positively charged sol whereas As_2S_3 is a negatively charged sol.

ILLUSTRATION 5.75

What is electrodialysis?

Sol. It is a process by which colloidal solutions containing ionic impurities are purified. The colloidal solution containing ionic impurities is placed in a bag of parchment paper in distilled water electric field. The ions come out through parchment paper and the sol is purified.

ILLUSTRATION 5.76

What is the main cause of charge on a colloidal solution?

Sol. The charge on the colloidal particles is due to the adsorption of common ions of the electrolyte on the surface of the colloidal particles, e.g., Fe^{3+} from $FeCl_3$ on the surface of $Fe(OH)_3$ particles.

ILLUSTRATION 5.77

Why do colloidal solutions exhibit Tyndall effect?

Sol. Colloidal solutions exhibit Tyndall effect because the size of the colloidal particles (10–1000 Å) is such that they can scatter light.

ILLUSTRATION 5.78

Define ultrafiltration.

Sol. In this process, colloidal solutions are purified by carrying out filtration through special types of graded filters called ultra-filters. Filter paper allows the passage of electrolyte but does not allow the passage of colloidal particles.

ILLUSTRATION 5.79

Which is not the characteristic of hydro-phobic sols?

a. They are highly susceptible to coagulation by addition of electrolytes.

b. They have nearly the same surface tension and viscosity as that of dispersion medium.

c. Their stability is due to both electric charge and salvation of the particles.

d. Sol particles can be seen under ultramicroscope.

Sol.

c. The stability is attributed to electric charge on the sol particles.

ILLUSTRATION 5.80

Hydrophilic gels, when placed in water, absorb liquid resulting in an increase of their volume. This process of swelling of gels takes place with

a. No change in volume
b. Net increase in volume
c. Net decrease in volume
d. Large reduction in volume

Sol. **c.** There will be net decrease in volume.

ILLUSTRATION 5.81

Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na_2SO_4, and Na_3PO_4 solutions. Their coagulating values will be in the order

a. $NaCl > Na_2SO_4 > Na_3PO_4$
b. $Na_2SO_4 > Na_3PO_4 > NaCl$
c. $Na_3PO_4 > Na_2SO_4 > NaCl$
d. $Na_2SO_4 > NaCl > Na_3PO_4$

Sol.

a. Since the sol particles migrate toward cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater is the valence of effective ion, smaller will be its coagulation value.

ILLUSTRATION 5.82

During electro-osmosis of $Fe(OH)_3$ sol

a. Sol particles move towards anode
b. Sol particles move towards cathode
c. The dispersion medium move towards anode
d. The sol particles do not move in either direction

Sol.

(c, d) In electro-osmosis, the sol particle are prevented from migration where as the dispersion medium migrates in the direction opposite to those of particles. Here the medium is negatively charged.

ILLUSTRATION 5.83

Which of the following ionic substances will be most effective in precipitating the sulphur sol?

a. KCl **b.** $BaCl_2$
c. $Fe_2(SO_4)_3$ **d.** Na_3PO_4

Sol.

c. The sulphor sol is negatively charged and would be coagulated most effectively by Al^{3+}.

ILLUSTRATION 5.84

The colligative property of a sol compared to the aqueous solution of glucose of same concentration will be

a. Much smaller **b.** Much higher
c. The same **d.** Slightly lower

Sol.

a. Molar concentration of a sol is much smaller than that in a true solution of same strength (g L^{-1}) due to much larger particles.

ILLUSTRATION 5.85

Electrolytes can cause coagulation as well as peptization of colloidal solution. Explain?

Sol. Electrolytes provide oppositely charged ions which can cause coagulation of colloidal solution. Electrolytes can cause peptization also, e.g., $FeCl_3$ can peptize $Fe(OH)_3$ precipitate because it gives excess of Fe^{3+} ions which get adsorbed on $Fe(OH)_3$ precipitates. This breaks up the precipitate into smaller particles of the size of colloid.

CONCEPT APPLICATION EXERCISE 5.2

1. What are enzymes? Write brief mechanism of enzyme catalysis?
2. Give the general method of preparation of sols.
3. Describe the methods for the purification of colloidal solution.
4. Describe the electrical properties of colloidal solution.
5. What is emulsion? Write its applications.
6. What is demulsification?
7. Describe the cleansing action of soap.
8. How are associated colloids different from macromolecular and multimolecular colloids?
9. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?
10. What happens when persistant dialysis of colloidal solution is carried out?
11. What type of building blocks are present in the structure of zeolites? What is this structure called?

12. What do x and m represent in the following expression? $(x/m) = KP^{1/n}$

13. Indicate a chemical reaction involving a homogeneous catalyst.

14. What type of substances form lyophobic sols?

15. How can we remove moisture from glass apparatus?

16. How is adsorption of a gas related to its critical temperature?

17. What are the different thermodynamical parameters that illustrate the mechanism of Adsorption?

18. Draw the following graphs. Do mention their slope and intercept, if can be calculated?

a. x/m vs p **b.** $\log \frac{x}{m}$ vs $\log p$

c. Physisorption isobar **d.** Chemisorption isobar

19. How does a solid catalyst enhance the rate of combination of gaseous molecule?

20. What is the role of diffusion in heterogeneous catalyst?

21. For soaps critical micelle concentration (CMC) is 10^{x} (min.) to 10^{y} (max.) mol/L. What is the value of x?

22. Twenty percent of the surface sites of a catalyst is occupied by nitrogen molecules. The density of surface sites is 6.023×10^{14} cm^{-2}. The total surface area is 1000 cm^2. The catalyst is heated to 300 K and nitrogen is completely desorbed into a pressure of 0.001 atm and volume of 2.46 cm^3. Calculate the number of sites occupied by nitrogen molecules.

23. One gram of charcoal adsorbs 100 ml of 0.5 M acetic acid to form a monolayer, and the molarity of acetic acid reduces to 0.49. Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. The surface area of charcoal is 3.01×10^2 m^2 g^{-1}.

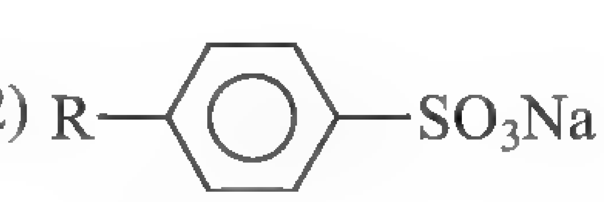
ANSWERS

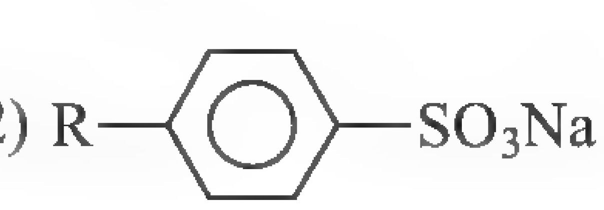
22. 2 **23.** 5×10^{19} m^2

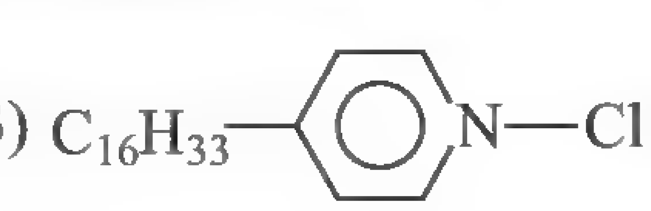
Exercises

Single Correct Answer Type

Adsorption

1. The effect of pressure on adsorption is high if
   (1) Temperature is low
   (2) Temperature is high
   (3) Temperature is neither very low nor very high
   (4) Charcoal piece is taken in place of charcoal powder
2. Which one of the following statements is wrong?
   (1) Physical adsorption of a gas is directly related to its critical temperature.
   (2) Chemical adsorption decreases regularly as the temperature is increased.
   (3) Adsorption is an exothermic process.
   (4) A solid with a rough surface is a better adsorbent than the same solid with a smooth surface.
3. Which of the following is true during adsorption?
   (1) ΔG, ΔH, and ΔS all are negative.
   (2) ΔG is negative, but ΔH and ΔS are positive.
   (3) ΔG and ΔH are negative, but ΔS is positive.
   (4) ΔG and ΔS are negative, but ΔH is positive.
4. Which one of the following statements is wrong about adsorption?
   (1) It is a selective and specific process.
   (2) It is a reversible process.
   (3) An increase in the gaseous adsorbate causes an increase in a adsorption. However, at high pressure, the adsorption becomes constant.
   (4) It is an endothermic process.
5. Adsorption is the phenomenon in which substance
   (1) Accumulates on the surface of the other substance
   (2) Goes into the body of the other substance
   (3) Remains close to the other substance
   (4) None is correct
6. Sorption is the term used when
   (1) Adsorption takes place
   (2) Absorption takes place
   (3) Both take place
   (4) Desorption takes place
7. In the adsorption of oxalic acid on activated charcoal, the activated charcoal is called
   (1) Adsorbent (2) Adsorbate
   (3) Adsorber (4) Absorber
8. There is desorption of physical adsorption when
   (1) Temperature is increased
   (2) Temperature is decreased
   (3) Pressure is increased
   (4) Concentration is increased
9. The rate of chemisorption:
   (1) Decreases with increase of pressure
   (2) Increases with increase of pressure
   (3) Is independent of pressure
   (4) Is independent of temperature
10. Which of the following is not a characteristic of chemisorption?
    (1) It is irreversible.
    (2) It is specific.
    (3) It is multilayer phenomenon.
    (4) Heat of adsorption is about –400 kJ.
11. Chromatography is a technique based on
    (1) Adsorption and then dispersion of solute
    (2) Absorption of solute
    (3) Hydration of solute
    (4) Evaporation of solute
12. Amount of gas adsorbed per gram of adsorbent increases with pressure, but after a certain limit is reached, adsorption becomes constant. It is where
    (1) Multilayers are formed
    (2) Desorption takes place
    (3) Temperature is increased
    (4) Adsorption also starts
13. Softening of hard water is done using sodium aluminium silicate (zeolite). This causes
    (1) Adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing $Na^{\oplus}$ ions.
    (2) Adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Al^{3+} ions.
    (3) Both (1) and (2) are true
    (4) None is true
14. Which of the following is/are true statements?
    (1) Water vapour is absorbed by anhydrous calcium chloride both adsorbed by silica gel.
    (2) NH_3 is absorbed by water but adsorbed by charcoal.
    (3) Sugar is decolourized by animal charcoal based on adsorption.
    (4) Water is absorbed by conc H_2SO_4.
15. Anionic surfactants are
    (1) $C_{15}H_{31}COONa$ (2) 

    (3) $C_{18}H_{37}NH_3Cl$ (4) All
16. Cationic surfactants are
    (1) $C_{17}H_{35}COONa$ (2) 

    (3) 

    (4) $C_{16}H_{33}N(CH_3)_3Cl$

17. Non-ionogenic surfactants are

(1) 

(2) $C_{17}H_{35}COONa$

(3) $C_nH_{2n+1}(OCH_2CH_2)_xOH$

(4) All

18. Freundlich equation for adsorption of gases (in amount of X g) on a solid (in amount of mg) at constant temperature can be expressed as

(1) $\log \frac{X}{m} = \log P + \frac{1}{n} \log K$

(2) $\log \frac{X}{m} = \log K + \frac{1}{n} \log P$

(3) $\frac{X}{m} \propto P^n$

(4) $\frac{X}{m} = \log P + \frac{1}{n} \log K$

19. Which of the following statements is incorrect regarding physisorption?

(1) It occurs because of van der Waals forces.

(2) Liquefiable gases are adsorbed more easily.

(3) Under high pressure it results surface.

(4) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive.

20. The equation of Langmuir adsorption isotherm under high pressure is:

(1) $\frac{x}{m} = \frac{a}{b}$ (2) $\frac{x}{m} = \frac{1}{ap}$

(3) $\frac{x}{m} = \frac{b}{a}$ (4) $\frac{x}{m} = ap$

21. Which of the following is a wrong form of Langmuir adsorption isotherm?

(1) $\frac{x}{m} = \frac{a}{b}$ (At high pressure)

(2) $\frac{x}{m} = \frac{ap}{b}$ (At high pressure)

(3) $\frac{x}{m} = ap$ (At very low pressure)

(4) $\frac{x}{m} = \frac{b}{a} + \frac{1}{ap}$ (At intermediate pressure)

22. For adsorption of a gas on a solid, the plot of $\log\left(\frac{x}{m}\right)$ *vs* $\log p$ is linear with slope equal to (n being whole number):

(1) $\log\ k$ (2) k

(3) n (4) $\frac{1}{n}$

23. 2.0 g of charcoal is placed in 100 mL of 0.05 M CH_3COOH to form an adsorbed mono-acidic layer of acetic acid molecules and thereby the molarity of CH_3COOH reduces to 0.49. The surface area of charcoal is 3×10^2 m^2 g ^{1}. The surface area of charcoal adsorbed by each mlecule of acetic acid is:

(1) 1.0×10^{-19} cm^2 (2) 1.0×10^{13} cm^2

(3) 1.0×10^{-18} cm^2 (4) 1.0×10^{-14} cm^2

24. In Langmuir's model of adsorption of a gas on a solid surafce,

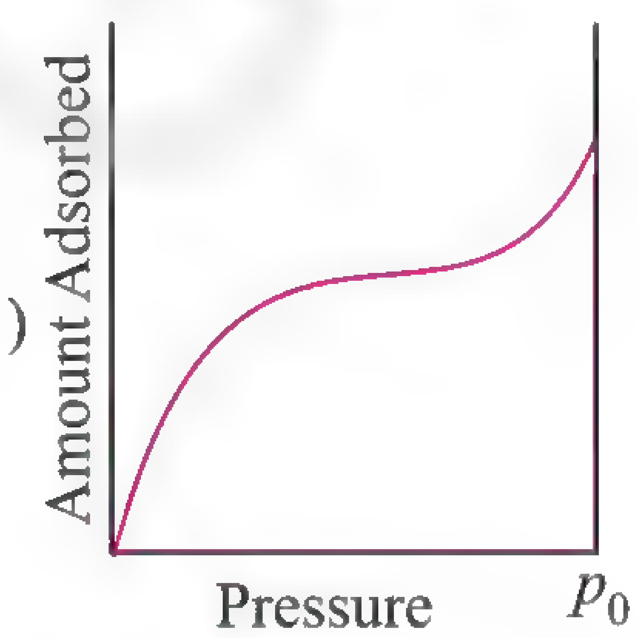
(1) The mass of gas striking a given area of surface is independent of the pressure of the gas.

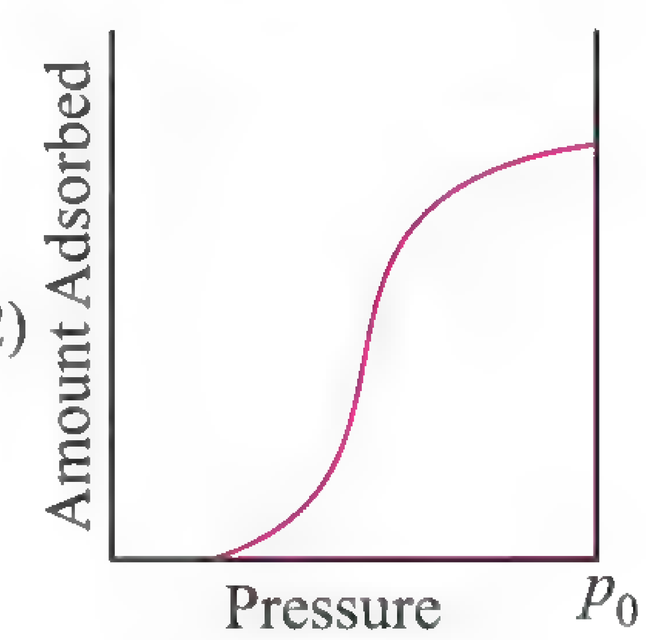
(2) The adsorption at a single site on the surface may involve multiple molecules at the same time.

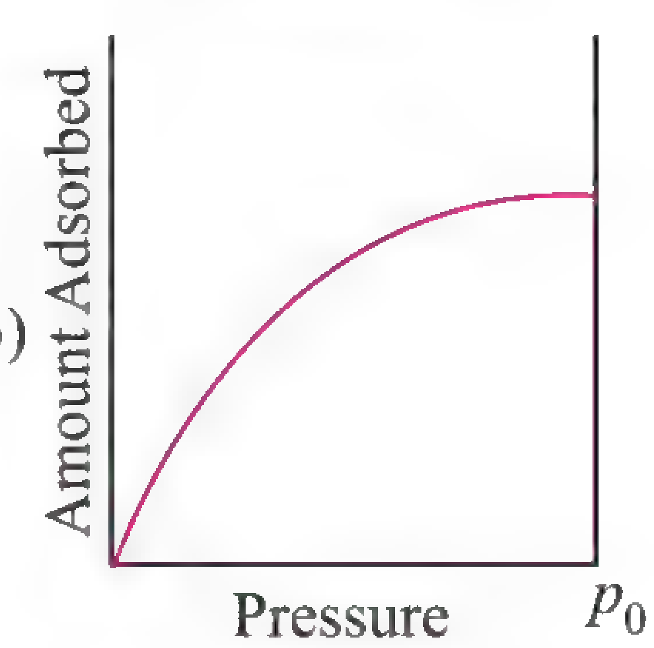
(3) The mass of gas striking a given area of surface is proportional to the pressure of the gas.

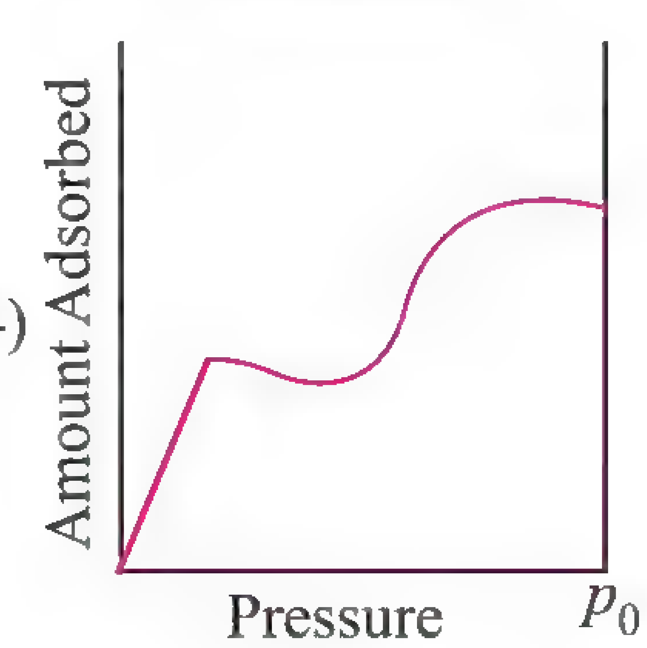
(4) The rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered.

25. From the following graphs, which two represent Langmuir Adsorption Isotherms?

(1) 

(2) 

(3) 

(4) 

26. If H_2 gas is made to absorb on a surface, then the fraction of surface area of adsorbent covered by gas molecules is proportional to:

(1) p^0 (2) p^2

(3) $p^{1/2}$ (4) p

27. Which is correct in case of van der Waals' adsorption?

(1) High temperature, high pressure

(2) Low temperature, high pressure

(3) Low temperature, low pressure

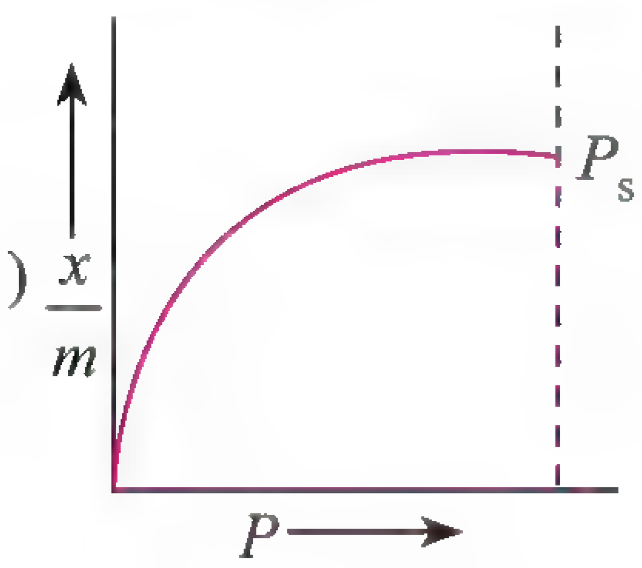
(4) High temperature, low pressure

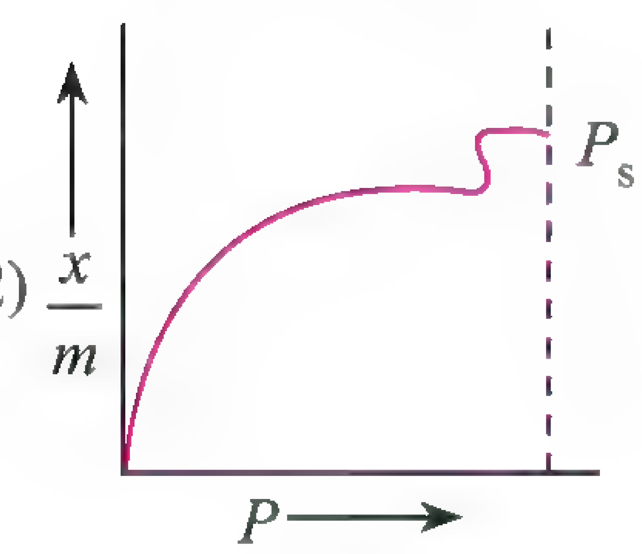
28. The most adsorbed gas on an activated charcoal is:

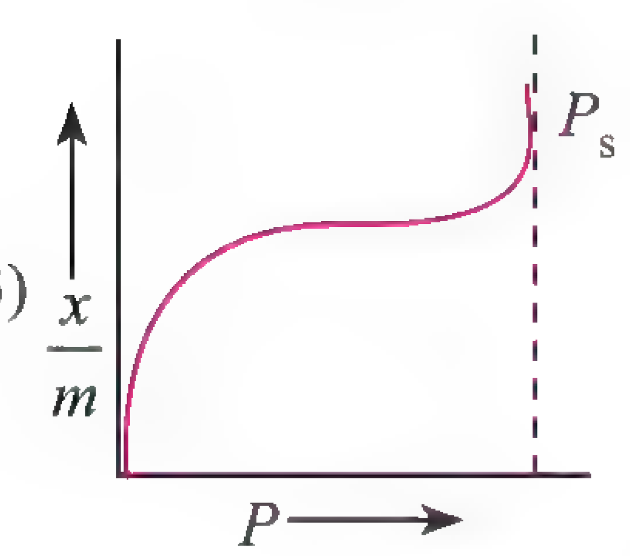
(1) CH_4 (2) H_2

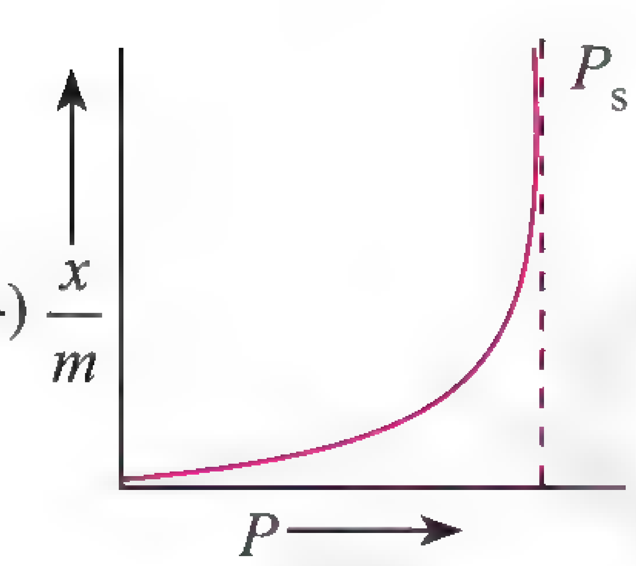
(3) CO_2 (4) N_2

29. Which of the following adsorption isotherms represents the adsorption of a gas by a solid involving multilayers of formation? (P_s = saturation pressure)

(1) 

(2) 

(3) 

(4) 

30. Which among the following statements is false?

(1) Increase of pressure increases the amount of adsorption.

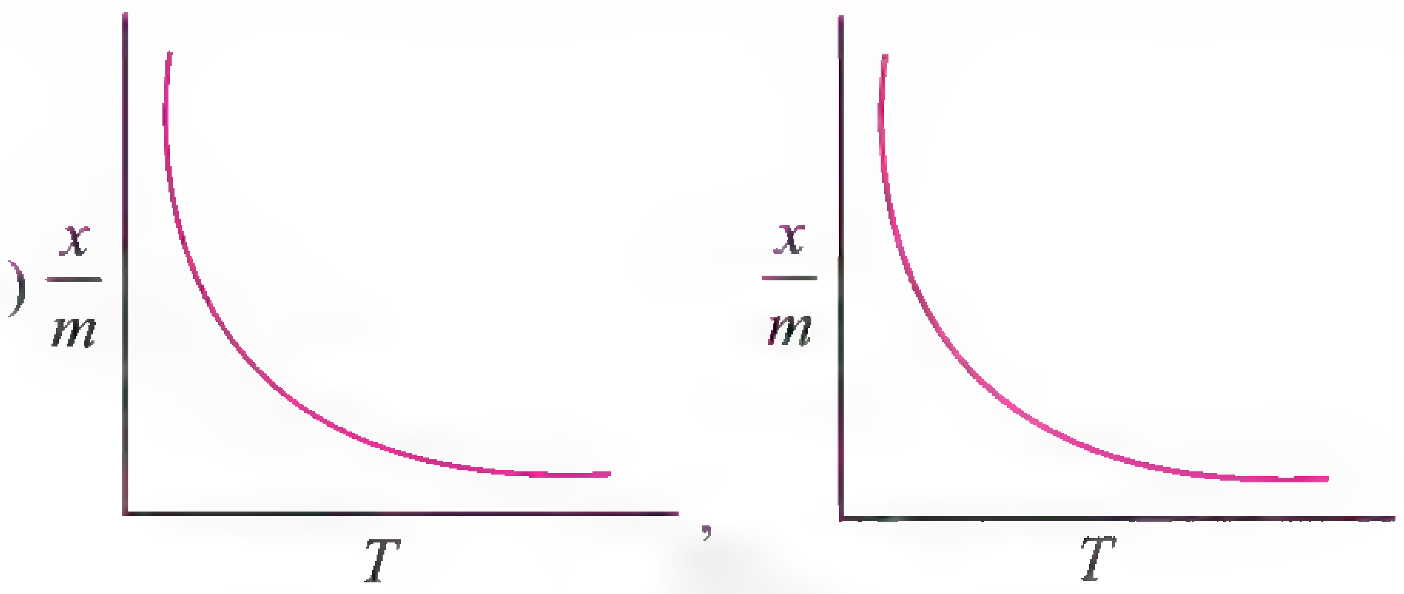
(2) Increase of temperature may decrease the amount of adsorption.

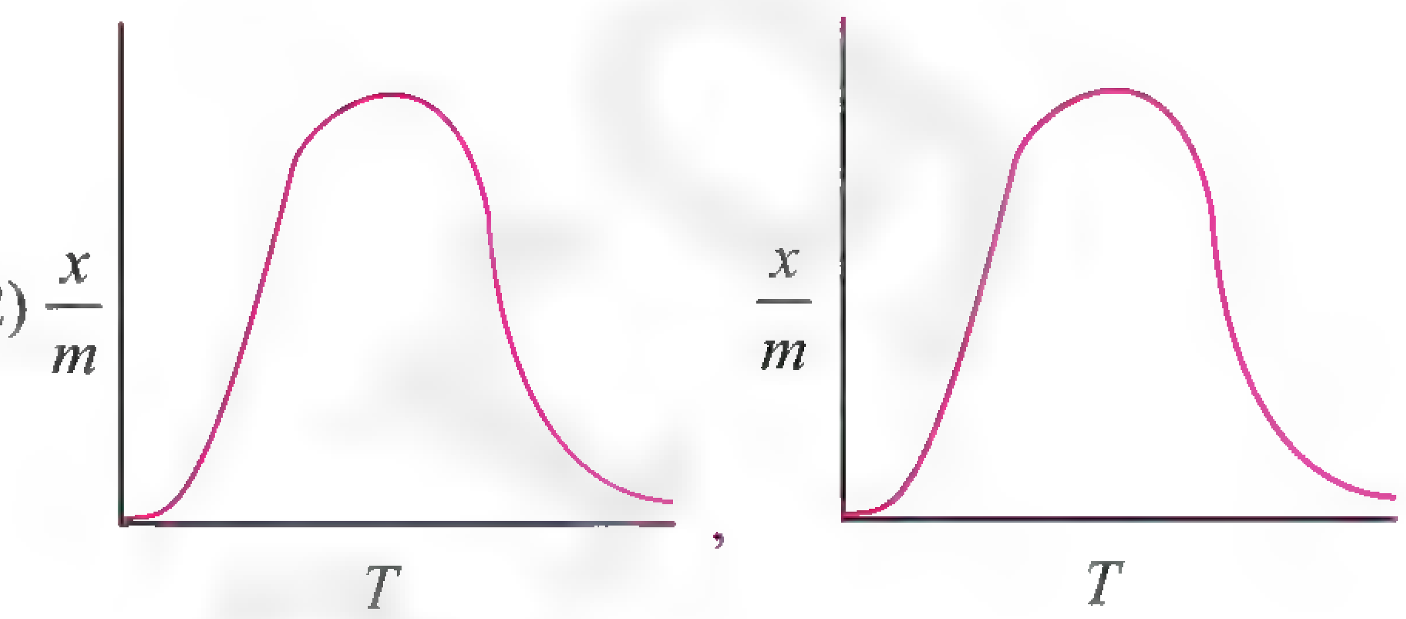
(3) Adsorption may be monolayered or multilayered.

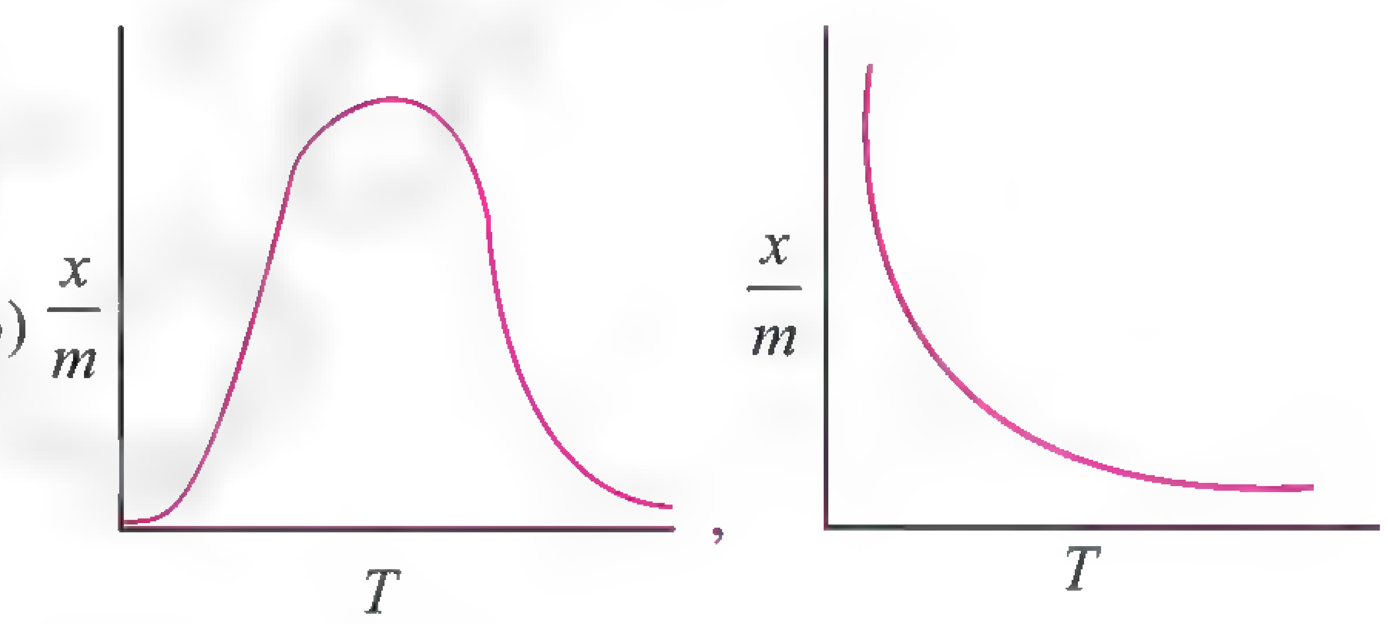
(4) Particle size of the adsorbent will not affect the amount of adsorption.

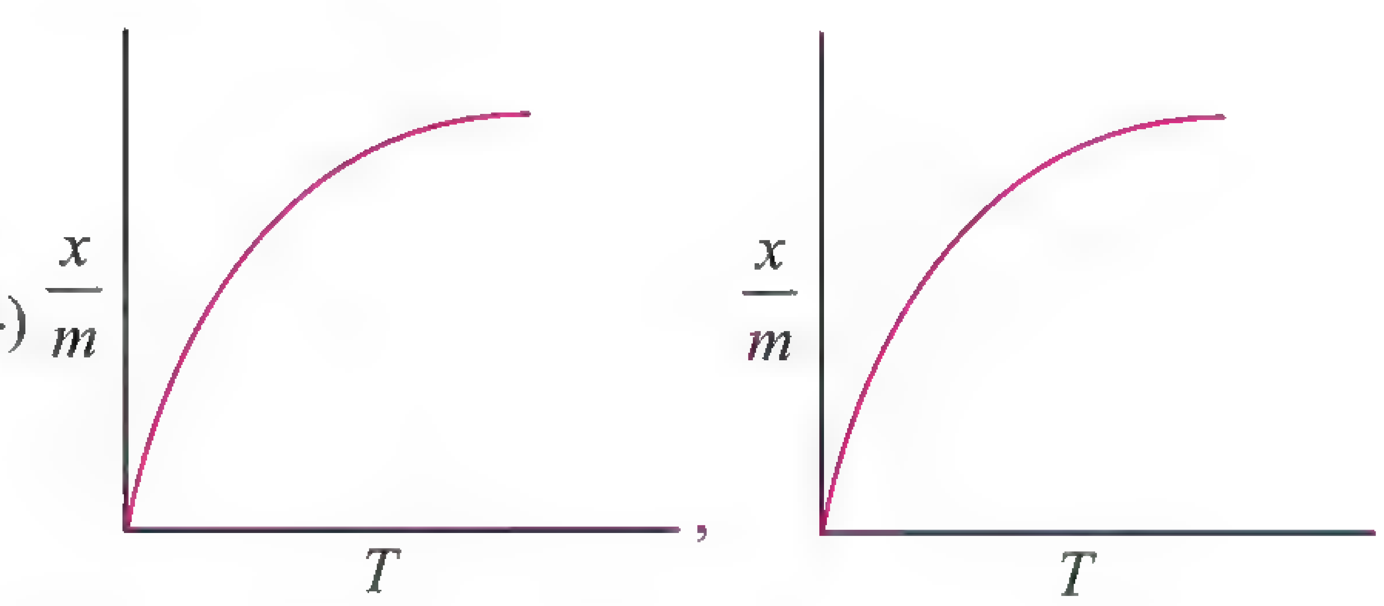
31. Select correct adsorption isobars for chemisorption and physisorption respectively:

(where $\frac{x}{m}$ = extent of adsorption, T = temperature)

(1) 

(2) 

(3) 

(4) 

32. Although, nitrogen does not adsorb on a surface at room temperature, it adsorbs on the surface at 83 K. Which one of the following statements is correct?

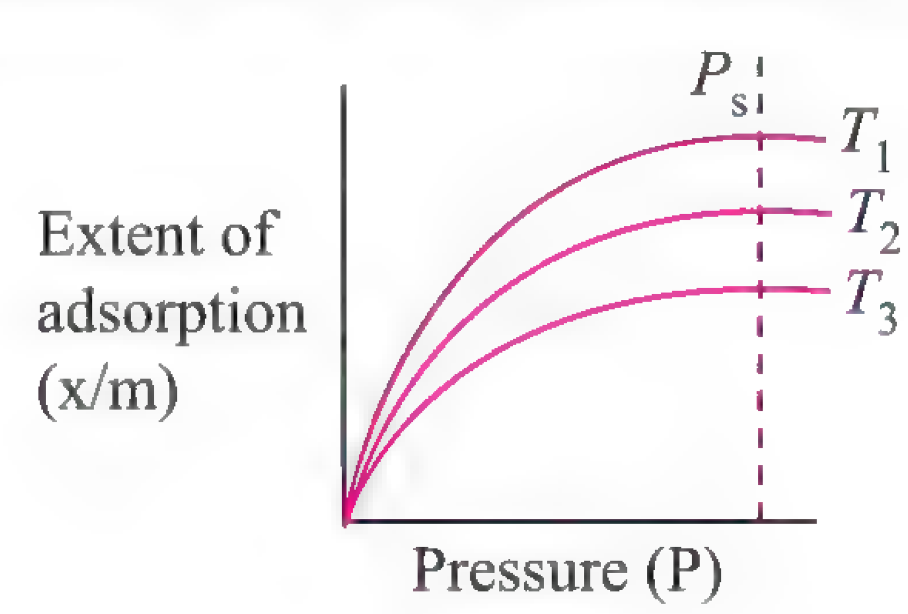
(1) At 83 K, there is formation of monolayer.

(2) At 83 K, nitrogen is adsorbed as atoms.

(3) At 83 K, nitrogen molecules are held by chemical bonds.

(4) At 83 K, there is formation of multimolecular layers.

33. For the graph below, select **correct** order of temperature?



(1) $T_1 > T_2 > T_3$ (2) $T_2 > T_3 > T_1$

(3) $T_3 > T_2 > T_1$ (4) $T_1 = T_2 = T_3$

Classification, Preparation and Properties of Colloidal Sol.

34. Zeta potential (or electrokinetic potential) is the

(1) Potential required to bring about coagulation of a colloidal sol.

(2) Potential required to give the particles a speed of 1 cm s^{-1} in the sol.
(3) Potential difference between fixed charged layer and the diffused layer having opposite charges.
(4) Potential energy of the colloidal particles.

35. Blue colour of the sky is due to
(1) Adsorption of light by dust particles
(2) Reflection of light by dust particles
(3) Scattering of light by dust particles
(4) Pressure of clouds which are a colloidal dispersion of water particles in air

36. Example of an intrinsic colloid is
(1) As_2S_3 sol (2) S sol
(3) Egg albumin (4) $Fe(OH)_3$ sol

37. Of which of the following colloidal systems, fog is an example?
(1) Liquid dispersed in gas (2) Gas dispersed in gas
(3) Solid dispersed in gas (4) Solid dispersed in liquid

38. 1 mol of [Ag] $Ag^{\oplus}$ sol is coagulated by
(1) 1 mol of KI
(2) 500 mL of 1 M K_2SO_4
(3) 300 mL of 1 M Na_3PO_4 solution
(4) 1 mol of AgI

39. Arsenic(III) sulphide forms a sol with a negative charge. Which of the following ionic substances should be most effective in coagulating the sol?
(1) KCl (2) $MgCl_2$ (3) $Al_2(SO_4)_3$ (4) Na_3PO_4

40. Aluminium hydroxide forms a positively charged sol. Which of the following ionic substances should be most effective in coagulating the sol?
(1) NaCl (2) $CaCl_2$ (3) $Fe_2(SO_4)_3$ (4) K_3PO_4

41. Brownian motion is a/an
(1) Electrical property (2) Mechanical property
(3) Optical property (4) Colligative property

42. The colligative property of a colloidal sol compared to the solution of non-electrolyte of same concentration will be
(1) Same (2) Higher
(3) Lower (4) Higher or lower

43. Which of the following can act as a protective colloid?
(1) Gelatin (2) Silica gel
(3) Oil-in-water emulsion (4) All correct

44. An emulsifier is an agent which
(1) Accelerates the dispersion
(2) Homogenizes an emulsion
(3) Stabilizes an emulsion
(4) Aids the flocculation of an emulsion

45. The stabilization of a dispersed phase in a lyophobic colloid is due to
(1) The adsorption of charged substances on dispersed phase.
(2) The large electro-kinetic potential developed in the colloid.
(3) The formation of an electrical layer between two phases.
(4) The viscosity of the medium.

46. The diameter of colloidal particle is of the order
(1) 10^{-3} m (2) 10^{-6} m
(3) 10^{-15} m (4) 10^{-7} m

47. The process of passing of a precipitate into colloidal solution on adding an electrolyte is called
(1) Dialysis (2) Peptization
(3) Electrophoresis (4) Electro-osmosis

48. Tyndall effect is not observed in
(1) Suspension (2) True solution
(3) Emulsions (4) Colloidal solution

49. The process of removing dissolved impurities from a colloidal system by means of diffusion through suitable membrane under the influence of an electric field is called
(1) Electro-osmosis (2) Electrodialysis
(3) Eleetrophoresis (4) Peptization

50. The migration of positively charged colloidal particles, under an electrical field, towards the cathode is called
(1) Cataphoresis (2) Electro-osmosis
(3) Sedimentation (4) Electrodialysis

51. Smoke is a dispersion of
(1) Gas in gas (2) Gas is solid
(3) Solid in gas (4) Liquid in gas

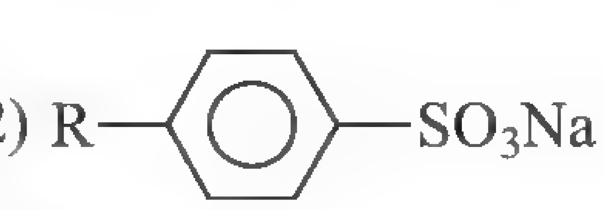
52. The colloidal sol of As_2S_3 prefers to adsorb
(1) $NO_3^{\ominus}$ (2) $K^{\oplus}$
(3) S^{2-} (4) $H^{\oplus}$

53. A freshly formed ppt of SnO_2 is peptized by a small amount of NaOH. These colloidal particles may be represented as
(1) $[SnO_2]SnO_3^{2-}; 2Na^{\oplus}$ (2) $[SnO_2]\ Sn^{4+}; O^{2-}$
(3) $[SnO_2]Na^{\oplus}; OH^{\ominus}$ (4) $[SnO_2]\ Sn^{4+}; OH^{\ominus}$

54. Smoke has generally blue tinge. It is due to
(1) Scattering (2) Coagulation
(3) Brownian motion (4) Electro-osmosis

55. Oil-soluble dye is mixed with water-in-oil emulsion, then
(1) Dispersion medium is coloured
(2) Dispersed phase is coloured
(3) Both coloured
(4) None is coloured

56. An oil-soluble dye is mixed with emulsion and the emulsion remains colourless. Then, it is
(1) O-in-W (2) W-in-O (3) O-in-O (4) W-in-W

57. There is no scum formation when hard water is being used. The washing powder can be
(1) $C_{17}H_{35}COONa$ (2) 
(3) Both (4) None

58. Micelles are
(1) Ideal solution (2) Associated colloids
(3) Adsorbed surfaces (4) Absorbent solutes

59. Compared to common colloidal sols micelles have:
(1) Higher colligative properties
(2) Lower colligative properties
(3) Same colligative properties
(4) None is true

60. Which one of the following statements is correct?
(1) Brownian movement is more pronounced for smaller particles than for bigger ones.
(2) Sols of metal sulphides are lyophilic.
(3) Hardy Schulze law states, the bigger the size of the ion, the greater is its coagulating power.
(4) One would expect charcoal to adsorb chlorine more strongly than hydrogen sulphide.

61. Gold number of a lyophilic sol is such a property that
(1) The larger its value, the greater is the peptizing power.
(2) The lower its value, the greater is the peptizing power.
(3) The lower its value, the greater is the protecting power.
(4) The larger its value, the greater is the protecting power.

62. Select the incorrect statement about micelles.
(1) They are associated.
(2) Surfactant molecules form micelles.
(3) They are formed above CMC and above the kraft temperature.
(4) Above CMC, the surfactant molecules undergo dissociation.

63. Select the incorrect statement:
(1) Micro emulsion and micellar solution are used to describe concentrated sufactant stabilized dispersion of water and hydrocarbons that are used to enhance petroleum recovery.
(2) Purple of cassius is Au sol. in water and is used to raise vitality in human system.
(3) Bredig's are method that cannot be used for the preparation of colloidal sol. of sodium.
(4) High charge density is the most important factor which gives rise to peculiar properties of colloids .

64. Select the incorrect statement:
(1) Brownian motion is more effective for small particles than the bigger ones
(2) Brownian motion is due to impact of molecules of the dispersion medium on the colloidal particles.
(3) Black diamonds are dispersion of solid in solid.
(4) Blood contains negative as well as positively charged particles.

65. Flocculating value of ion depends on:
(1) The shape of flocculating ion.
(2) The amount of flocculating ion.
(3) Nature of the charge on the flocculating ion.
(4) Both, the nature and magnitude of the charge of the flocculating ion.

66. Which of the following will have highest coagulating power for As_2S_3 colloid ?
(1) Al^{3+} (2) $Na^{\oplus}$
(3) SO_4^{2-} (4) PO_4^{3-}

67. 1 mol of [AgI] $Ag^{\oplus}$ can be coagulated by:
(1) 1 mol of $AgNO_3$ (2) 1/2 mol of $AgNO_3$
(3) 2/3 mol of $AgNO_3$ (4) None of these

68. The coagulation of 100 mL of colloidal solution of gold is completely prevented by addition of 0.25 g of a substance "X" to it before addition of 1 mL of 10% NaCl solution. The gold number of "X" is:
(1) 0.25 (2) 25
(3) 250 (4) 2.5

69. Which of the following mixture will lead to the formation of negatively charged colloid $[AgI]I^{\ominus}$?
(1) 50 mL of 0.1 M $AgNO_3$ + 50 mL of 0.1 M KI
(2) 50 mL of 0.1 M $AgNO_3$ + 50 mL of 0.2 M KI
(3) 50 mL of 0.2 M $AgNO_3$ + 50 mL of 0.1 M KI
(4) 50 mL of 0.2 M $AgNO_3$ + 50 mL of 0.2 M KI

70. Arsenous sulphide sol is prepared by passing H_2S through arsenous oxide solution. the charge developed on the particles is due to adsorption of:
(1) $H^{\oplus}$ (2) S^{2-}
(3) $\overset{\ominus}{O}H$ (4) O^{2-}

71. Select incorrect statement:
(1) Gold sol is multimolecular coloid.
(2) Large number of particles of a substance aggregate together and formed multimolecular colloids.
(3) Metal sulphides are lyophobic colloids.
(4) Sulphur sol is multimolecular colloid and hydrophilic in nature.

72. Select incorrect statement:
(1) Soap and detergent lower the interfacial surface tension between oil and water.
(2) Basic principle of peptization is reverse of coagulation.
(3) Soap and detergent are used as emulsifiers.
(4) Lyophilic sols need stabilizing agent.

73. For the coagulation of 50 mL of ferric hydroxide sol, 10 mL of 0.5 M KCl is required. What is the coagulation value of KCl ?
(1) 5 (2) 10
(3) 100 (4) None of these

74. 100 mL of 0.6 M acetic acid is shaken with 2 g activated carbon. The final concentration of the solution after adsorption is 0.5 M. What is the amount of acetic acid adsorbed per gram of carbon ?
(1) 0.6 g (2) 0.3 g
(3) 1.2 g (4) None of these

Catalysis

75. Catalyst increases the rate by

(1) Decreasing E_a (2) Increasing E_a

(3) Decreasing pressure (4) Increasing entropy

76. Which of the following catalyst is used during the hydrogenation of oil?

(1) Fe (2) Ni

(3) Pt (4) Mo

77. Which of the following is present at the time of cracking of hydrocarbons?

(1) Copper (2) Zeolite

(3) Nickel (4) Molybdenum

78. Which is not the correct statement for a catalyst?

(1) It does not alter E_a.

(2) The surface of a catalyst adsorbs reactants.

(3) Catalyst may form intermediates with reactants.

(4) Action of enzyme catalyst is always specific.

79. Match column A (catalyst) with column B (process)

A	B
1. SiO_2	**I.** Cracking of Hydrocarbon
2. Pt	**II.** of benzene
3. Zeolites	**III.** Automobile converter

(1) 1→I, 2→II, 3→III (2) 1→III, 2→II, 3→1

(3) 1→II, 2→III, 3→I (4) 1→III, 2→I, 3→II

80. Catalyst used in polymerization of ethene is:

(1) $TiCl_4$ and AlR_3 (2) Fe, Co

(3) H_3PO_4 (4) Zeolites

81. Which is/are correct statements about the role of a catalyst in a reaction?

(1) It is reactant in a rate-determining step and then a product of some subsequent step.

(2) It provides an alternate mechanism with a lower energy of activation.

(3) It increases the rate of chemical reaction but does not itself undergo a permanent change during the course of the reaction.

(4) All of these.

82. Energy of activation of forward and backward reaction are equal in cases (numerical values) where

(1) $\Delta H = 0$

(2) No catalyst present

(3) $\Delta S = 0$

(4) Stoichiometry is the mechanism

83. Select the correct statement.

(1) Homogeneous catalysis occur at the interface of phases.

(2) Hydrolysis of protein in stomach and in intestine takes place due to the action of enzyme trypsin in stomach and pepsin in intestine

(3) ZsM - 5 is used to convert toluene to benzene.

(4) Negative catalyst physically changes at the end of reaction.

84. In which of the following reactions heterogeneous catalysis is involved?

i. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

ii. $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

iii. $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

iv. $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$

(1) (ii), (iii) (2) (ii), (iii) and (iv)

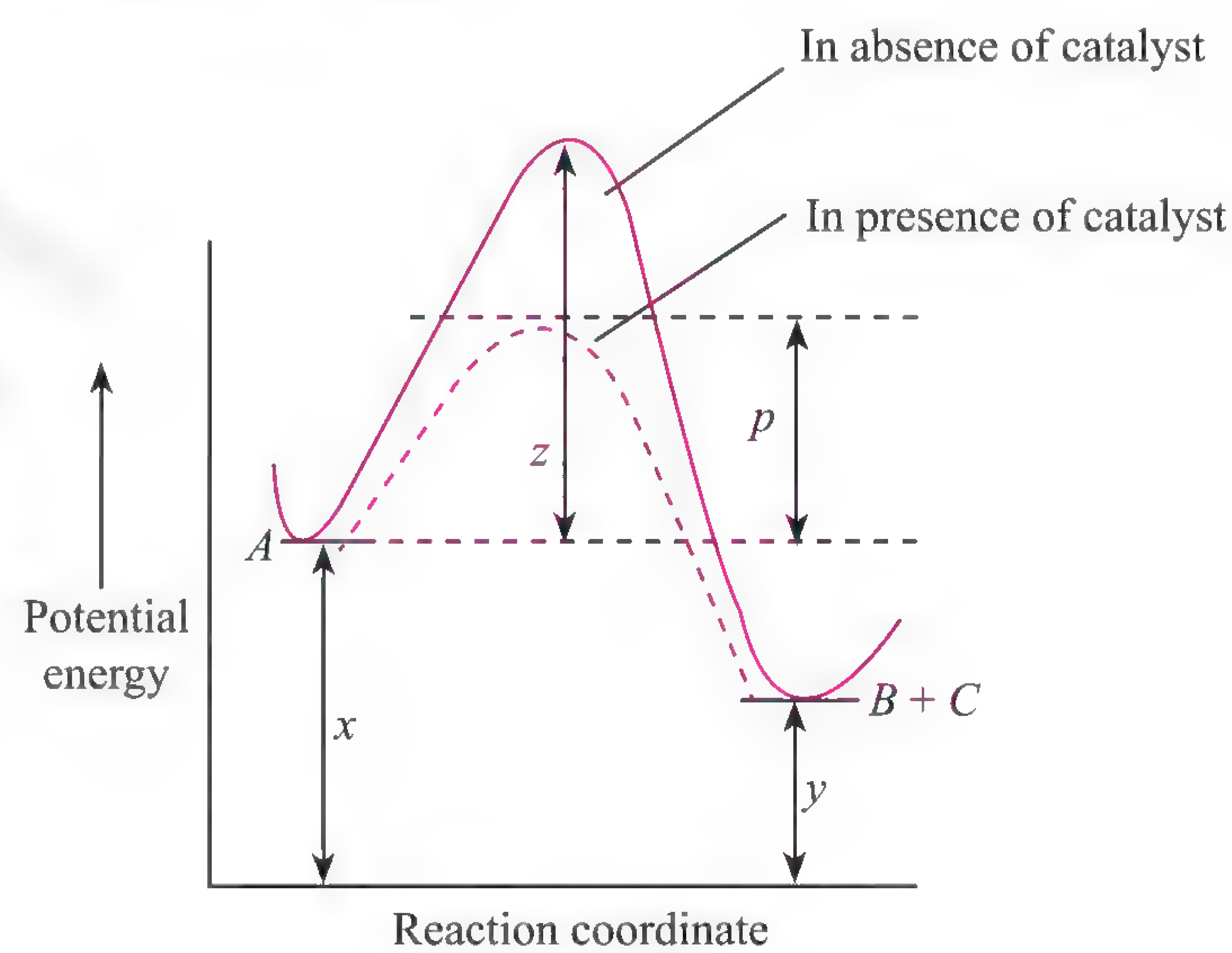
(3) (i), (ii) and (iii) (4) (iv)

85. Air can oxidize sodium sulphite in aqueous solution but cannot do so in the case of sodium arsenite. If however, air is passed through a solution containing both sodium sulphite and sodium arsenite then both are oxidized. This is an example of:

(1) Positive catalysis (2) Negative catalysis

(3) Induced catalysis (4) Auto-catalysis

86. For the reaction A → B + C; the energy profile diagram is given in the figure:



What is the decrease in energy of activation in presence of catalyst ?

(1) z (2) $z - p$

(3) $y - z$ (4) $z - x$

87. The rate of a certain biochemical reaction catalysed by an enzyme in human body is 10^4 times faster than when it is carried out in the laboratory. The activation energy of this reaction:

(1) Is zero

(2) Is different in both the cases

(3) Is the same in both the cases

(4) None of the above

88. A catalytic poison renders the catalyst ineffective because:

(1) It is preferentially adsorbed on the catalyst.

(2) It adsorbs the molecules of the reactants.

(3) It combines chemically with the catalyst.
(4) It combines chemically with one of the reactants.

89. An inhibitor is essentially:
(2) A negative catalyst (2) A heterogeneous catalyst
(3) An auto catalyst (4) A homogeneous catalyst

90. Identify the correct statement regarding enzymes:
(1) Enzymes are specific biological catalysts that normally works at high temperature
(2) Enzymes are normally heterogeneous catalysts which decrease the reaction rate
(3) Enzymes are specific biological catalysts with low molar masses
(4) Enzymes are specific biological catalysts that are very specific in nature

Miscellaneous

91. The gold numbers of protective colloids A, B, C, and D are 0.04, 0.002, 10, and 25, respectively. The protective powers of A, B, C, and D are in the order
(1) A > B > C > D (2) B > A > C > D
(3) D > C > A > B (4) D > C > B > A

92. When 6×10^{-5} g of a protective colloid was added to 20 mL of a standard gold sol, the precipitation of latter was just prevented on addition of 2 mL of 10% NaCl solution. The gold number of a protective colloid is
(1) 3 (2) 3×10^{-5} (3) 0.06 (4) 0.03

93. In an experiment, addition of 4.0 mL of 0.005 M $BaCl_2$ to 16.0 mL of arsenious sulphide sol just causes the complete coagulation in 2 h. The flocculating value of the effective ion is:
(1) $Cl^{\ominus}$, 1.0 (2) $Cl^{\ominus}$, 2.0 (3) Ba^{2+}, 1.0 (4) Ba^{2+}, 0.5

94. A freshly obtained precipitate of SnO_2 is peptized by little of KOH to give a sol. The sol particles may be represented as
(1) $[SnO_2]K^{\oplus}$ (2) $[SnO_2]OH^{\ominus}$
(3) $[SnO_2]Sn^{4+}$ (4) $[SnO_2]SnO_3^{2-}$

Multiple Correct Answers Type

Adsorption

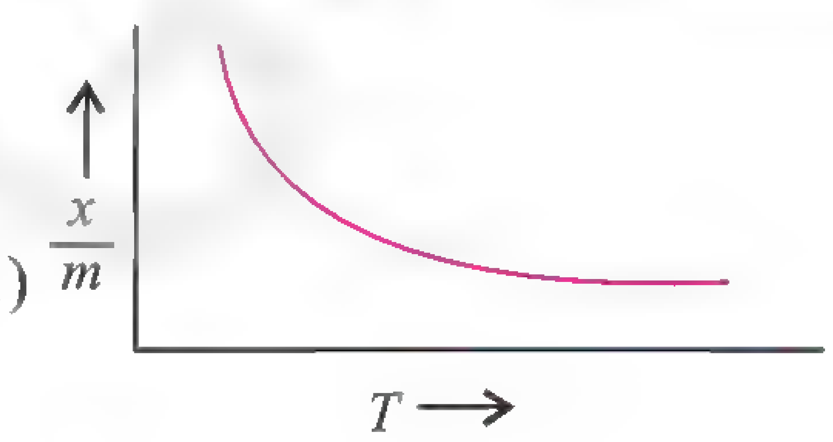
1. Which of the following increase(s) the activation of a solid adsorbent?
(1) Polishing the surface of the solid adsorbent.
(2) Subdividing the solid adsorbent.
(3) Blowing superheated steam through the porous adsorbent.
(4) Adsorption at very low pressure.

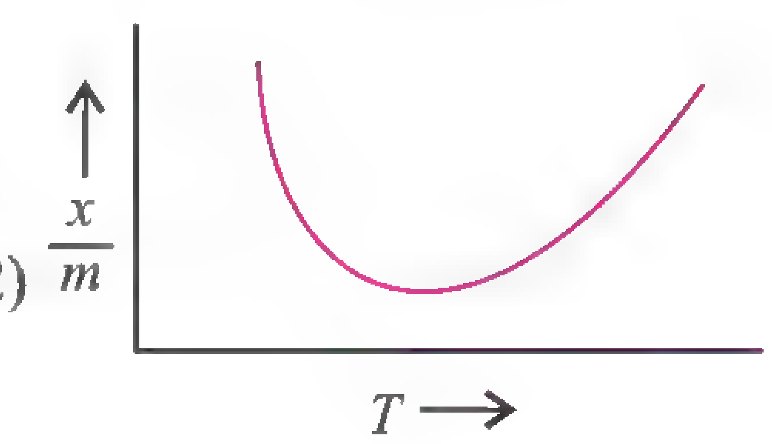
2. Which of the following statements is/are correct?
(1) Physical adsorption is multilayer, non-directional, and non-specific.
(2) In some cases, solvent may be adsorbed in preference to the solute on the surface of the adsorbent.
(3) Chemical adsorption increases with increase in temperature.
(4) Due to adsorption, surface energy increases.

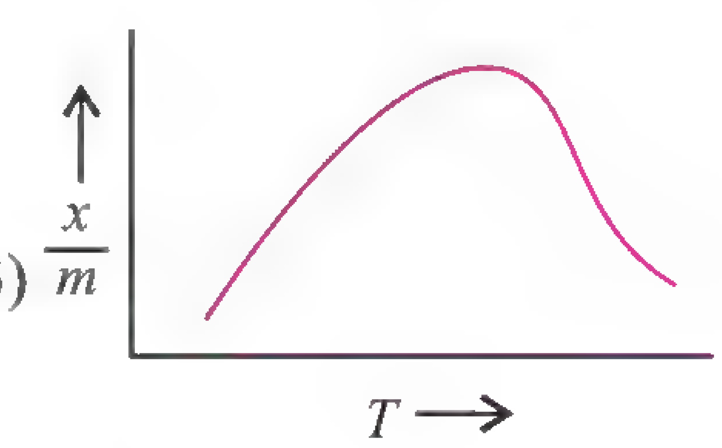
3. Which one of the following is/are correct statement for physisorption?
(1) It is a reversible process.
(2) It requires less heat of adsorption.
(3) It requires activation energy.
(4) It takes place at low temperature.

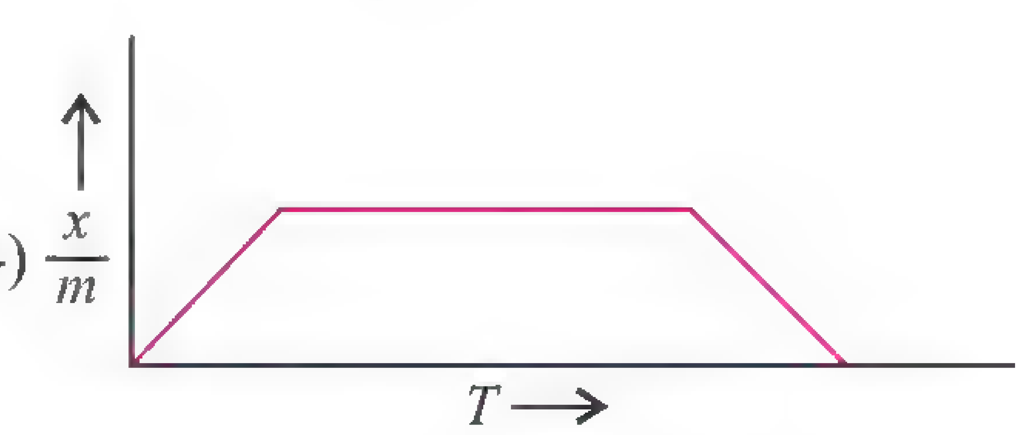
4. Which of the following statements is/are correct?
(1) Increase of pressure increases the amount of adsorption.
(2) Increase of temperature may decrease the amount of adsorption.
(3) The adsorption may be monolayered or multilayered.
(4) Particle size of the adsorbent will not affect the amount of adsorption.

5. Which is not the adsorption isobar for chemisorption?

(1) 

(2) 

(3) 

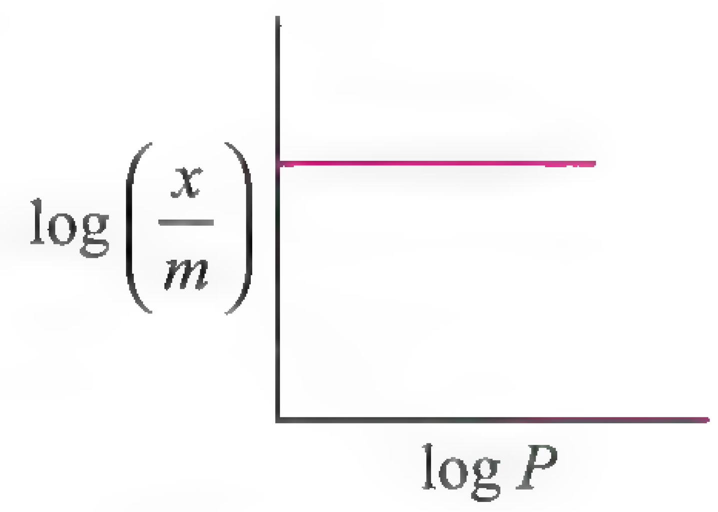
(4) 

6. Which of the following is/are application(s) of adsorption?
(1) De-ionization of water
(2) Gas masks
(3) Hygroscopic nature of $CaCl_2$
(4) Heterogeneous catalysis

7. Select the correct statement(s) among the following:
(1) At 83 K, N_2 is physisorped on the surface of iron.
(2) At 772 K and above N_2 is chemisorped on the iron surface.
(3) Activation energy is +ve in case of physisorption and zero in case of chemisorption.
(4) Activation energy is zero in case of physisorption and +ve in case of chemisorption.

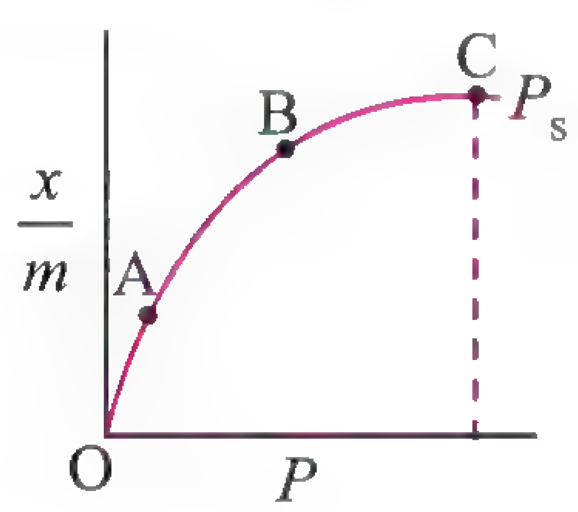
8. Select the correct statement(s):
   (1) Physical adsorption is reversible, has low heat of adsorption
   (2) Physical adsorption forms unimolecular layer and takes place at low temperature and decreases with increase in temperature
   (3) Physical adsorption is due to van der Waal's forces.
   (4) Emulsifiers do not work on the principle of adsorption

9. Adsorption isotherm of $\log\left(\frac{x}{m}\right)$ and $\log P$ was found of the type :



   This is incorrect when:
   (1) $P = 0$ (2) $P = 1$
   (3) $\frac{1}{n} = 1$ (4) $P < 1$

10. In the given isotherm select the **correct** statement:



   (1) $\frac{x}{m} \propto P^{1/n}$ along OA
   (2) $\frac{x}{m} \propto P^0$ when point B is reached
   (3) $\frac{x}{m}$ does not increase rapidly with pressure along BC due to less surface area available for adsorption
   (4) Nature of isotherm is different for two gases for same adsorbent

11. If adsorption of a gas on a solid is limited to monolayer formation, then which of the following statement(s) is/are true?
   (1) At low pressures, $\frac{x}{m}$ varies proportionately with p
   (2) At moderate pressures, $\frac{x}{m}$ varies less than proportionately with p
   (3) At hogh pressures, $\frac{x}{m}$ becomes independent of p
   (4) At high pressures, $\frac{x}{m}$ varies more than proportionately with p

12. Select the correct statement(s):
   (1) Physisorption is favoured by low temperature
   (2) Chemisorption is favoured by very high temperature because the process is endothermic
   (3) Chemisorption increases with increase in temperature owing to high activation energy
   (4) Oxygen adsorbed by charcoal can be desorbed by lowering pressure and temperature

Classification, Preparation and Properties of Colloidal Sol.

13. Which of the following is/are correctly matched?
   (1) Butter–gel (2) Milk–emulsion
   (3) Fog–aerosol (4) Dust–solid sol

14. Which of the following is/are elastic gel?
   (1) Gelatin (2) Silicic acid
   (3) Agar agar (4) Starch

15. Which of the following is/are negatively charged sol?
   (1) Gold sol (2) Prussian blue dye
   (3) Haemoglobin (4) Starch

16. Which of the following is/are aerosols?
   (1) Smoke (2) Milk (3) Butter (4) Fog

17. Which of the following is/are lyophobic colloids?
   (1) Gold sol (2) As_2S_3 sol
   (3) $Fe(OH)_3$ sol (4) Starch sol

18. Which of the following is/are not correctly matched?
   (1) Emulsion–curd (2) Foam–mist
   (3) Aerosol–smoke (4) Solid sol–cake

19. Which of the following electrolytes will not be most effective in the coagulation of gold sol?
   (1) $NaNO_3$ (2) $K_4[Fe(CN)_6]$
   (3) Na_3PO_4 (4) $MgCl_2$

20. Which of the following are macromolecular colloids?
   (1) Starch (2) Soap
   (3) Detergent (4) Cellulose

21. Isoelectric point is the pH at which colloidal particles
   (1) Coagulate
   (2) Become electrically neutral.
   (3) Can move toward either electrodes
   (4) None of these

22. Tyndall effect is applicable when
   (1) The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
   (2) The diameter of the dispersed particles is much smaller than the wavelength of the light used.
   (3) The refractive indices of the dispersed phase and the dispersion medium must be same.
   (4) The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude.

23. Multimolecular colloids are present in
   (1) Sol of sulphur (2) Sol of protein
   (3) Sol of gold (4) Soap solution

24. Select the correct statement(s).
   (1) Aerosol is a colloidal solution of liquid in gas while gel is a colloidal solution of solid in liquid.
   (2) Foam is a colloidal solution of gas in liquid while emulsion is a colloidal solution of liquid in liquid

(3) Starch, gelatin and gum are lyophilic in nature
(4) At CMC, the surfactant molecules undergo aggregation, micelle formation and reduction in surface tension of water.

25. Select the incorrect statement(s):
(1) Electrophoresis, Brownian movement and maxwell distribution are the properties of colloidal sols.
(2) Peptisation, electrophoresis at high potential and freezing can destroy the emulsion
(3) Mechanical disintegration method is used for the preperation of colloidal graphite and printing ink.
(4) Mechanical disintegration method is suitable when dispersion medium is an organic liquid

26. Which of the following statements is/are true?
(1) Flocculation value is inversely proportional to coagulating power
(2) Colloidal silica is protective colloid
(3) Alum is used for cleaning muddy water
(4) Gelatin is added in ice cream, it acts as an emulsifier.

27. Which of the following statements is/are **correct**?
(1) Mixing two oppositely charged sols neutralizes their charges and stabilizes the colloid
(2) Presence of equal and similar charges on colloidal particles provides stability to the colloids
(3) Any amount of dispersed liquid can be added to emulsion without destabilizing it
(4) Brownian movement stabilizes sols.

Catalysis

28. Which of the following statements is/are wrong?
(1) Zeolites are hydrated aluminosilicates which can be used as shape-selective catalysts.
(2) Enzymes show maximum activity when pH is either very low or very high.
(3) Enzymes show maximum activity at room temperature (20–25°C)
(4) Chemically, all enzymes are globular proteins.

29. Which of the following statements is/are not correct?
(1) A catalyst always increases the speed of a reaction.
(2) A catalyst does not take part in the reaction.
(3) A catalyst may affect the nature of the products formed.
(4) A catalyst is always an external substance added to the reaction mixture.

30. Which of the following belong(s) to the family of enzymes?
(1) Lipase (2) Pepsin (3) Ptylin (4) Cellulose

31. Which of the following is/are not possible in case of auto-catalysis?
(1) Reactant catalysis
(2) Heat produced in the reaction catalysis
(3) Product catalysis
(4) Solvent catalysis

32. Which of the following is/are the characteristic of a catalyst?
(1) It changes equilibrium point.
(2) It alter the rate of reaction.
(3) It initiates the reaction.
(4) It increases the average KE of molecules

33. Which one of the followings is/are an example of homogeneous catalysis?
(1) Formation of SO_3 in the chamber process.
(2) Formation of SO_3 in the contact process.
(3) Hydrolysis of an ester in the presence of acid.
(4) Decomposition of $KClO_3$ in the presence of MnO_2.

34. Efficiency of the catalyst does not depend on its?
(1) Molecular weight (2) Number of free valencies
(3) Physical state (4) Amount used

35. Which of the following statements is/are correct in the case of heterogeneous catalyst?
(1) The catalyst lowers the energy of activation.
(2) The catalyst actually forms a compound with the reactant.
(3) The surface of the catalyst plays a very important role.
(4) There is no change in the energy of activation.

36. Select the correct statements:
(1) Heterogeneous catalyst lowers the energy of activation and reactant molecules are adsorbed on the surface of the catalyst
(2) Catalyst changes physically and quantitatively
(3) Ni is used in the hydrogenation of oil and thermite process does not involve any catalyst
(4) The decomposition of H_2O_2, is slowed down by the addition of small amount of acetamide which acts as poison

37. Which act(s) as negative catalyst?
(1) Lead tetraethyl as antiknock compound
(2) Glycerol in decomposition of H_2O_2
(3) Ethanol in oxidation of chloroform
(4) None of the above

38. Which of the following statement(s) is/are **correct** about solid catalyst?
(1) Same reactants may give different products by using different catalysts
(2) Catalyst does not change ΔH of reaction
(3) Catalyst is required in large quantities to catalyse reaction
(4) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption.

Linked Comprehension Type

Paragraph 1

A chemist studied the phenomenon of adsorption by putting blood charcoal in KCl solution. He observed difference in the behaviour with dilute KCl solution and with concentrated KCl solution. He

also studied the adsorption of different gases on solid adsorbent and the effect of temperature on adsorption. He put forward a mathematical relationship relating x/m with equilibrium pressure.

1. Which of the following is correct?
   (1) Adsorption is always exothermic?
   (2) Adsorption is always endothermic.
   (3) Physical adsorption is endothermic whereas chemisorption is exothermic.
   (4) Chemical adsorption is endothermic whereas physical adsorption is exothermic.
2. Which of the following plot will be linear? (More than one correct)
   (1) Plot of log x/m versus P
   (2) Plot of m/x versus $1/P$
   (3) Plot of log $\dfrac{P}{m/m}$ versus P
   (4) Plot of log m/x versus log P
3. The correct order of the adsorption of gases studied will be
   (1) $NH_3 > SO_2 > CO_2 > HCl$
   (2) $CO_2 > SO_2 > NH_3 > HCl$
   (3) $SO_2 > NH_3 > HCl > CO_2$
   (4) $HCl > SO_2 > NH_3 > CO_2$
4. Which of the following result is observed with the experiment of KCl solution?
   (1) Dilute KCl solution shows no adsorption whereas concentrated KCl shows adsorption.
   (2) Concentrated KCl solution shows positive adsorption whereas dilute KCl solution shows negative adsorption.
   (3) Concentrated KCl solution shows no adsorption whereas dilute KCl solution shows adsorption.
   (4) Dilute KCl solution shows positive adsorption whereas concentrated KCl solution shows negative adsorption.

Paragraph 2

Emulsions are also called the colloidal solutions in which the disperse phase as well as dispersion medium are liquids. It may be oil-in-water or water-in-oil type. Emulsifiers can be used to stabilize the emulsion. Soaps, detergents, proteins, and gums are used as emulsifiers.

5. Which of the following examples is/are oil-in-water-type emulsion?
   (1) Ink (2) Detergent (3) Soap (4) Milk
6. Emulsion can be destroyed by (more than one correct)
   (1) The addition of emulsifier which tends to form another emulsion
   (2) Electrophoresis with high potential
   (3) Freezing
   (4) All
7. Butter is an emulsion of type
   (1) Water in oil (2) Oil in water
   (3) None (4) Both (1) and (2)
8. Addition of lyophilic solution to the emulsion forms
   (1) A protective film around the dispersed phase
   (2) A protective film around the dispersion medium.
   (3) An aerosol
   (4) True solution
9. Which of the following is homogeneous?
   (1) Milk (2) Paint (3) Shampoo (4) All

Paragraph 3

There are certain substances which behave as normal, strong electrolyte at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called micelles. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC) and a characteristic temperature.

10. Micelles are
    (1) Emulsion-cum-gel (2) Adsorbed catalyst
    (3) Associated colloids (4) Ideal solutions
11. Micelles are formed only
    (1) Above CMC and above the Kraft temperature
    (2) Below CMC and the Kraft temperature
    (3) Above CMC and below the Kraft temperature
    (4) Below CMC and above the Kraft temperature
12. Above CMC, the surfactant molecules undergo (more than one correct)
    (1) Aggregation (2) Micelles formation
    (3) Dissociation (4) All
13. What type of molecules form micelles?
    (1) Non-polar molecules
    (2) Polar molecules
    (3) Surfactant molecules
    (4) Salt of weak acid and weak base
14. Micelles are used in
    (1) Detergents (2) Petroleum recovery
    (3) Magnetic separation (4) All of these

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1.

	Column I		Column II
a.	Dispersion of $Al(OH)_3$ by small quantity of $AlCl_3$	p.	Macromolecular colloid
b.	Addition of large quantity of $AlCl_3$ in (a)	q.	Selective adsorption
c.	Solution of haemoglobin in water	r.	Flocculation
d.	Chromatographic seperation of components of a solution	s.	Peptization

2.

	Column I		Column II
a.	Gold number	p.	Solvent heating
b.	Lyophobic	q.	Coagulation
c.	Butter	r.	Protective colloids
d.	Hardy Schulze rule	s.	Solvent
e.	Micelles	t.	Associated colloids
		u.	An emulsion

3.

	Column I		Column II
a.	Purple of cassius	p.	Gel
b.	Cheese	q.	Gold sol
c.	Dialysis	r.	Robert Brown
d.	Brownian movement	s.	Hydrophilic
e.	Water-loving colloids	t.	Purification of colloidal solutions

4.

	Column I		Column II
a.	Liquid dispersed in gas	p.	Emulsifying agent
b.	Tyndall effect	q.	Aerosol
c.	Hydrophobic	r.	Ultramicroscope
d.	Coagulation	s.	Irreversible
e.	Electrophoresis	t.	Sewage disposal
f.	Soap	u.	Smoke precipitator

5.

	Column I		Column II
a.	Activated charcoal	p.	A device to adsorb poisonous gases
b.	$x/m = KP^{1/n}$	q.	One of the adsorbents
c.	For humidity control	r.	Silica gel
d.	Gas masks	s.	Freundlich adsorption isotherm

6.

	Column I		Column II
a.	Physisorption	p.	Multimolecular
b.	Chemisorption	q.	High heat of activation
c.	Activated adsorption	r.	High temperature required
d.	Desorption	s.	Low pressure required
e.	Electro-osmosis	t.	Determination of charge on colloidal particles

7.

	Column I		Column II
a.	Placing silica gel in water vapour	p.	Enzymatic catalysis
b.	Placing anhydrous $CaCl_2$ in water vapour	q.	Occlusion
c.	Placing finely divided nickel in a closed vessel containing H_2 gas	r.	Adsorption
d.	Shaking dilute KCl solution with blood charcoal	s.	Absorption
e.	Conversion of proteins into amino acids	t.	Negative adsorption

Numerical Value Type

1. From the given following sol how many can coagulate the haemoglobin sol?
   $Fe(OH)_3$, $Ca(OH)_2$, $Al(OH)_3$, starch, clay, As_2S_3, CdS, basic dye.
   (1) 1 (2) 3 (3) 4 (4) 8
2. From the given following sol how many can coagulate silica acid sol?
   $Fe(OH)_3$, $Ca(OH)_2$, $Al(OH)_3$, Starch, Clay, As_2S_3, CdS, Basic dye.
   (1) 4 (2) 3 (3) 2 (4) 8
3. For the coagulation of 500 mL of arsenious sulphide sol, 2 mL of 1M NaCl is required.What is the flocculation value of NaCl?
   (1) 3 (2) 2 (3) 5 (4) 4
4. The coagulation of 100 mL of a colloidal sol of gold is completely prevented by addition of 0.03 g of haemoglobin to it before adding 1 mL of 10% NaCl solution. Calculate the gold number of haemoglobin.
   (1) 4 (2) 8 (3) 3 (4) 9
5. The gold number of gelatin is 0.01. Calculate the amount of gelatin to be added to 1000 mL of a colloidal sol of gold to prevent its coagulation, before adding 1 mL of 10% NaCl solution.
   (1) 2 (2) 1 (3) 4 (4) 5
6. 526.3 mL of 0.5 m HCl is shaken with 0.5 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 m. The amount of adsorption (x/m) is
   (1) 3 (2) 6 (3) 8 (4) 4
7. In an experiment, addition of 5.0 mL, of 0.006 M $BaCl_2$ to 10.0 mL of arsenic sulphite sol just causes the complete coagulation in 34 h. The flocculating value of the effective ion is :
   (1) 2 (2) 3 (3) 4 (4) 5
8. In an adsorption experiment, a graph between log (x/m) versus log P was found to be linear with a slope of 45°. The intercept on the y axis was found to be 0.301. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 3.0 atm.
   (1) 4 (2) 2 (3) 6 (4) 8

Archives

JEE ADVANCED

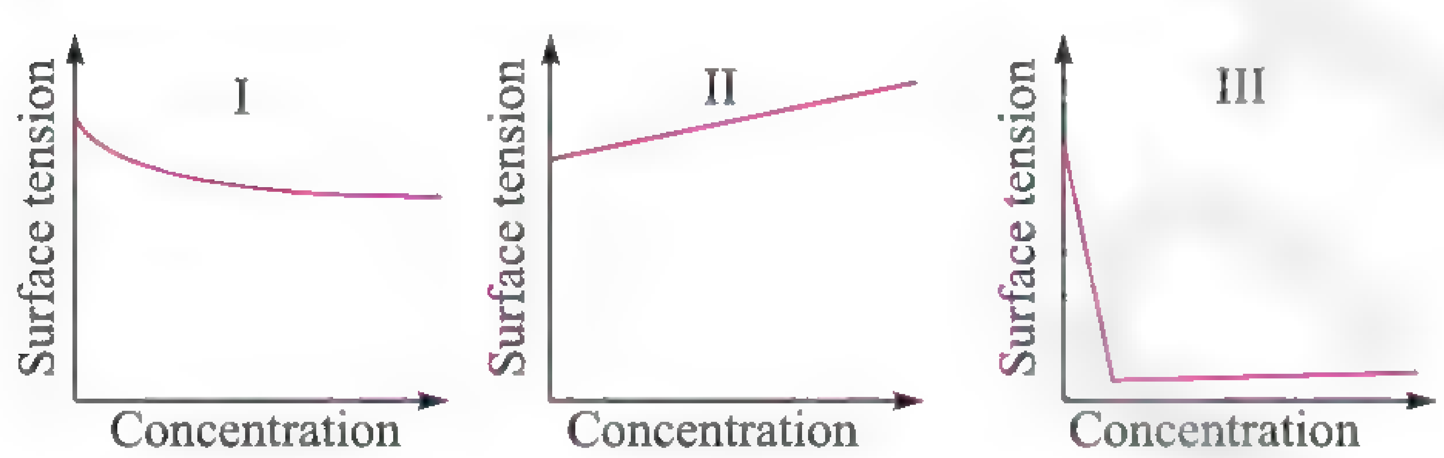
Single Correct Answer Type

1. Among the following electrolytes, which is the most effective coagulating agent for Sb_2S_3 solution?
   (1) Na_2SO_4 (2) $CaCl_2$
   (3) $Al_2(SO_4)_3$ (4) NH_4Cl
   (IIT-JEE 2009)

2. The coagulating power of electrolytes having ions $Na^{\oplus}$, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order :
   (1) $Na^{\oplus} < Ba^{2+} < Al^{3+}$ (2) $Ba^{2+} < Na^{\oplus} < Al^{3+}$
   (3) $Al^{3+} < Na^{\oplus} < Ba^{2+}$ (4) $Al^{3+} < Ba^{2+} < Na^{\oplus}$
   (JEE Advanced 2013)

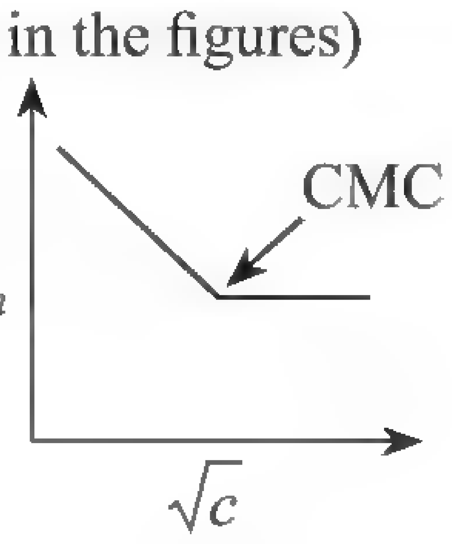
3. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
   (1) The adsorption requires activation at 25°C
   (2) The adsorption is accomanied by a decrease in enthalpy
   (3) The adsorption increases with increase of temperature.
   (4) The adsorption is irreversible
   (JEE Advanced 2013)

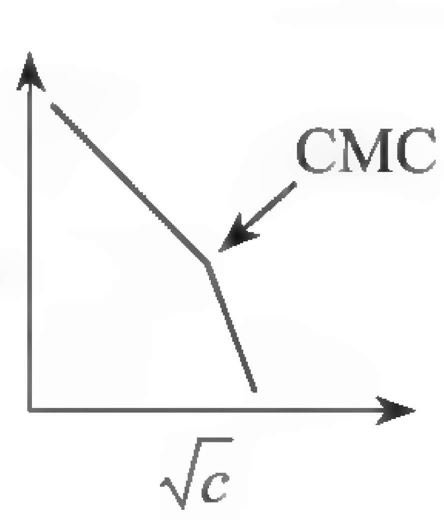
4. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solution of KCl, CH_3OH and $CH_3(CH_2)_{11}\ OSO_3^-\ Na^+$ at room temperature. The correct assignment of the sketches is

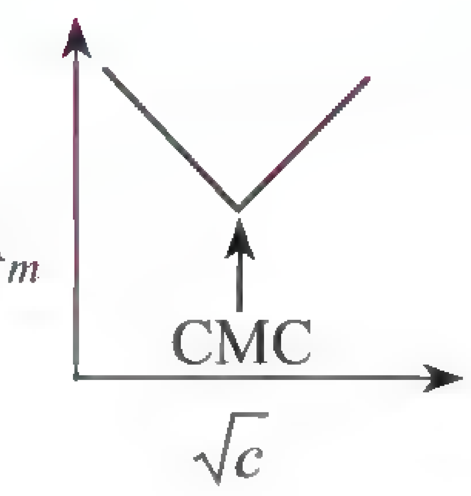


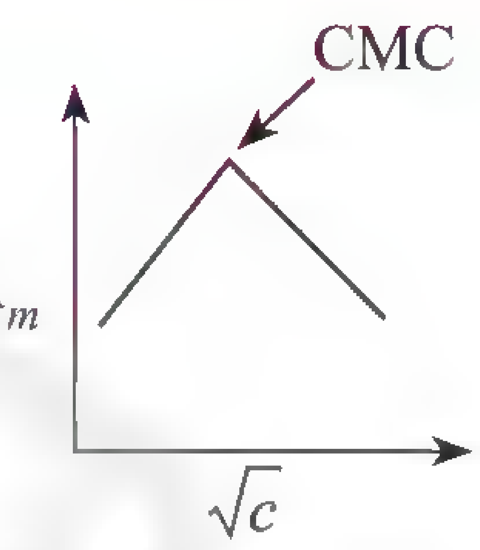
   (1) I : KCl II : CH_3OH III : $CH_3(CH_2)_{11}\ OSO_3^-\ Na^+$
   (2) I : $CH_3(CH_2)_{11}\ OSO_3^-\ Na^+$ II : CH_3OH III : KCl
   (3) I : KCl II : $CH_3(CH_2)_{11}\ OSO_3^-\ Na^+$ III : CH_3OH
   (4) I : CH_3OH II : KCl III : $CH_3(CH_2)_{11}\ OSO_3^-\ Na^+$
   (JEE Advanced 2016)

5. Molar conductivity (Λ_m) of aqueous solution of sodium stearate, which behaves as a strong electrolyte, is recorded at varying concentrations (c) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution?
   (critical micelle concentration (CMC) is marked with an arrow in the figures)

   (1) Λ_m


   (2) Λ_m


   (3) Λ_m


   (4) Λ_m


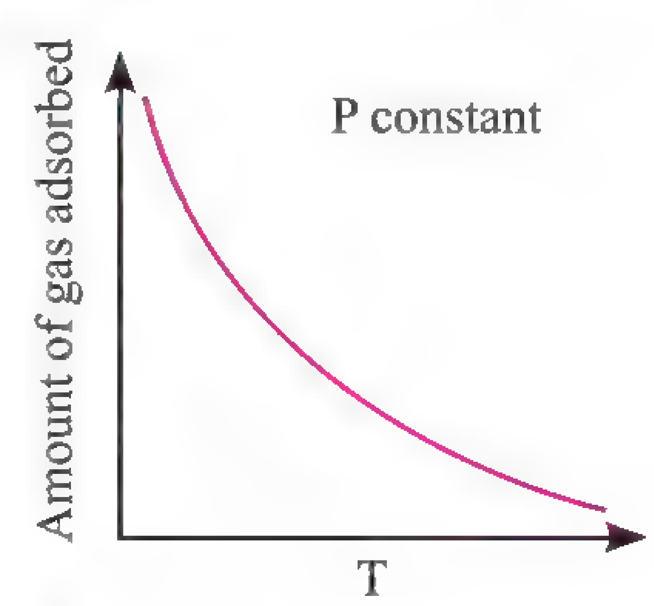
   (JEE Advanced 2019)

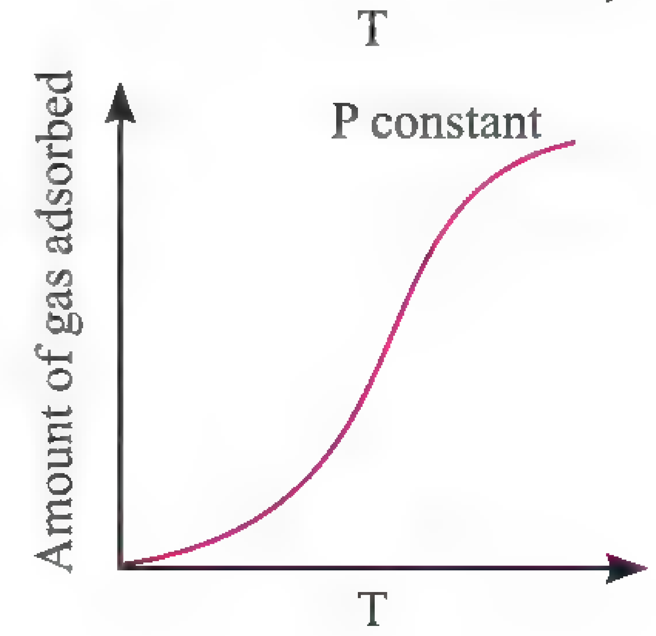
Multiple Correct Answers Type

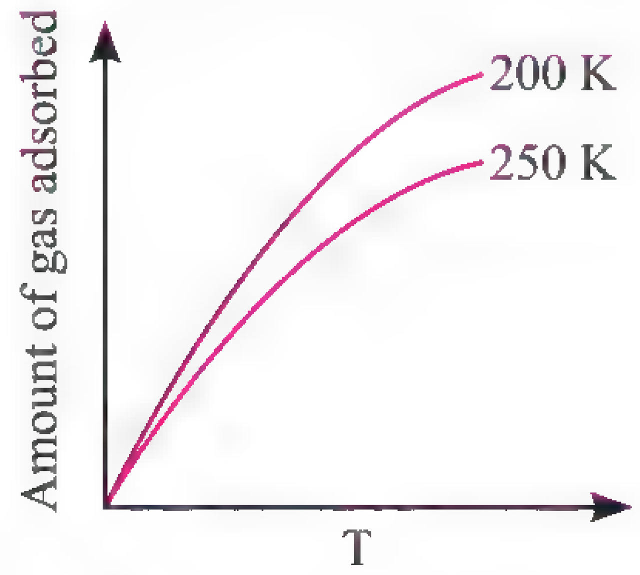
1. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is(are)
   (1) Adsorption is always exothermic.
   (2) Physisorption may transform into chemisorption at high temperature.
   (3) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
   (4) Chemisorption is more exothermic than physisorption; however, it is very slow due to higher energy of activation. **(IIT-JEE 2011)**

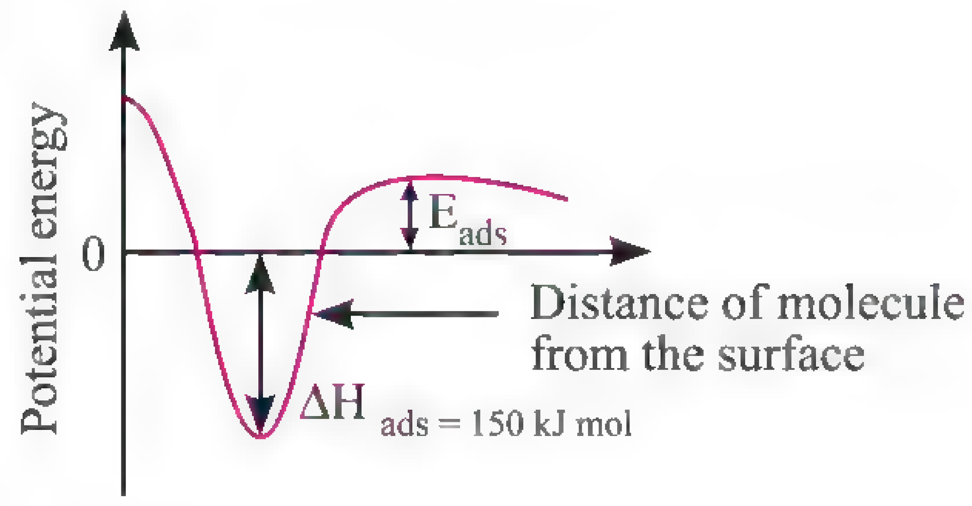
2. Choose the correct reason(s) for the stability of the lyophobic colloidal particles.
   (1) Preferential adsorption of ions on their surface from the solution.
   (2) Preferential adsorption of solvent on their surface from the solution.
   (3) Attraction between different particles having opposite charges on their surface.
   (4) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.
   (IIT-JEE 2012)

3. The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is/are correct?

I.


II.


III. 

IV. 

(1) I is physisorption and II is chemisorption.
(2) IV is chemisorption and II is chemisorption.
(3) I is physisorption and III is chemisorption.
(4) IV is chemisorption and III is chemisorption.

(IIT-JEE 2012)

4. The correct statement(s) about surface properties is(are)
   (1) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
   (2) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature
   (3) Cloud is an emulsion type of coloid in which liquid is dispersed phase and gas is dispersion medium
   (4) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution **(JEE Advanced 2017)**
5. The correct statement(s) related to colloids is(are)
   (1) The process of precipitating colloidal sol by an electrolyte is called peptization.
   (2) Colloidal solution freezes at higher temperature than the true solution at the same concentration.
   (3) Surfactants form micelle above critical micelle concentration (CMC). CMC depends on temperature.
   (4) Micelles are macromolecular colloids.

(JEE Advanced 2021)

Answers Key

EXERCISES

Single Correct Answer Type

1. (1) **2.** (2) **3.** (1) **4.** (4) **5.** (1)
6. (3) **7.** (1) **8.** (1) **9.** (2) **10.** (3)
11. (1) **12.** (1) **13.** (1) **14.** (3) **15.** (1,2)
16. (3,4) **17.** (3) **18.** (2) **19.** (4) **20.** (1)
21. (1) **22.** (4) **23.** (4) **24.** (3) **25.** (2)
26. (3) **27.** (2) **28.** (3) **29.** (1) **30.** (4)
31. (3) **32.** (4) **33.** (1) **34.** (3) **35.** (3)
36. (3) **37.** (1) **38.** (1,2) **39.** (3) **40.** (4)
41. (2) **42.** (3) **43.** (1) **44.** (2) **45.** (3)
46. (4) **47.** (2) **48.** (2) **49.** (2) **50.** (1)
51. (3) **52.** (3) **53.** (1) **54.** (1) **55.** (1)
56. (1) **57.** (2) **58.** (2) **59.** (2) **60.** (1)
61. (3) **62.** (4) **63.** (4) **64.** (4) **65.** (4)
66. (1) **67.** (4) **68.** (2) **69.** (2) **70.** (2)
71. (4) **72.** (4) **73.** (3) **74.** (2) **75.** (1,3)
76. (2) **77.** (2) **78.** (1) **79.** (3) **80.** (2)
81. (4) **82.** (1) **83.** (4) **84.** (1) **85.** (3)
86. (2) **87.** (2) **88.** (1) **89.** (1) **90.** (4)
91. (2) **92.** (4) **93.** (3) **94.** (4)

Multiple Correct Answers Type

1. (2, 3) **2.** (1, 2) **3.** (1, 2, 4)
4. (1, 2, 3) **5.** (1, 2, 4) **6.** (1, 2, 4)
7. (1, 2, 4) **8.** (1, 3) **9.** (1, 2, 4)
10. (1, 3, 4) **11.** (1, 2, 3) **12.** (1, 3, 4)
13. (1, 2, 3) **14.** (1, 3, 4) **15.** (1, 4)
16. (1, 4) **17.** (1, 2, 3) **18.** (1, 2, 4)
19. (1, 2, 3) **20.** (1, 4) **21.** (1, 2, 3)
22. (1, 4) **23.** (1, 3) **24.** (1, 3, 4)
25. (1, 2, 4) **26.** (1, 3, 4) **27.** (2, 4)
28. (1, 2, 3) **29.** (1, 2, 4) **30.** (1, 2, 3)
31. (1, 2, 4) **32.** (2, 3, 4) **33.** (1, 3, 4)
34. (1, 3, 4) **35.** (1, 2, 3) **36.** (1, 3)
37. (1, 2, 3) **38.** (1, 2)

Linked Comprehension Type

1. (1) **2.** (1,2,3) **3.** (3) **4.** (2) **5.** (4)
6. (2,3) **7.** (1) **8.** (1) **9.** (1) **10.** (1)
11. (1) **12.** (1,2) **13.** (3) **14.** (1)

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	s	r	p	—	—	—
2.	r	s	u	q	t	—
3.	q	p	t	r	s	—
4.	q	r	s	t	u	p
5.	q	s	r	p	—	—
6.	p	q, r	q, r	s	t	—
7.	r	s	q	t	p	—

Numerical Value Type

1. (3) **2.** (1) **3.** (4) **4.** (3) **5.** (2)
6. (4) **7.** (1) **8.** (3)

ARCHIVES

JEE Advanced

Single Correct Answer Type

1. (3) **2.** (1) **3.** (2) **4.** (4) **5.** (2)

Multiple Correct Answers Type

1. (1, 2, 4) **2.** (1, 4) **3.** (1, 3)
4. (2, 4) **5.** (2, 3)

Chapter 5

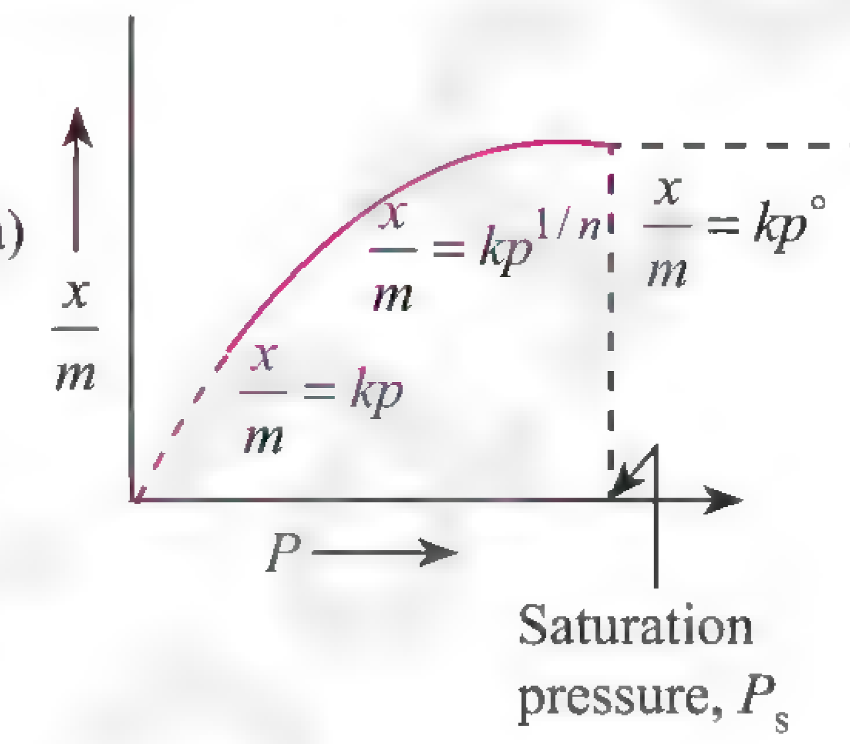
Concept Application Exercises

Exercise 5.1

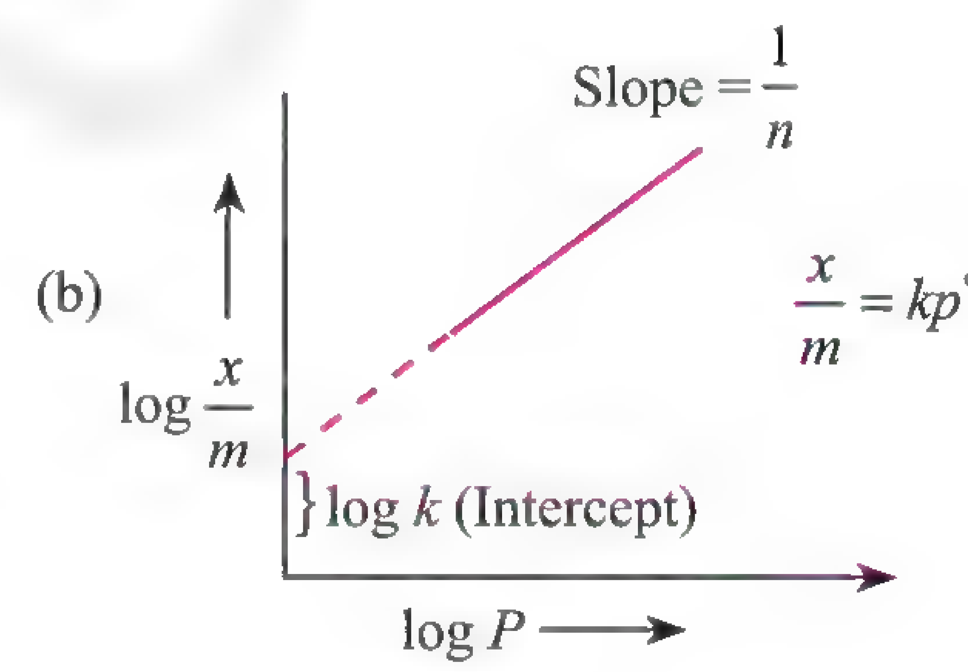
1. Refer to Section 5.2.
2. Refer to Section 5.2.4.
3. Higher the critical temperature of a gas, greater is the ease of liquefication of gas, i.e., larger are the van der Waals forces of attraction. Therefore, greater is the adsorption.
4. Refer to Section 5.2.
5. Refer to Section 5.2.3.
6. Adsorption is a surface phenomenon.
7. Finely divided substance results in larger surface area and hence larger adsorption occurs.
8. Refer to Section 5.2.3.

Exercise 5.2

1. Refer to Section 5.7.
2. Refer to Section 5.5.2.
3. Refer to Section 5.5.3.
4. Refer to Section 5.5.4.
5. Refer to Section 5.6.
6. The process of breaking an emulsion to yield the constituents liquids is called demulsification.
7. Refer to Section 5.5.1.
8. Difference between associated colloids and multimolecular and macromolecular colloids. Multimolecular colloids are formed by the aggregation of a large number of simple molecules (e.g., S_8), macromolecular colloids are due to large size of the molecules themselves (e.g., starch), so large that their size lies in the colloidal range. However, associated colloids are formed by electrolytes so that they dissociate into ions and these ions associate together to form ionic micelles whose size lies in the colloidal range, e.g., soaps. This happens above a particular concentration (called critical micellization concentration) and above a particular temperature called Kraft temperature.
9. Refer to Section 5.5.1.
10. The stability of a colloidal sol is due to the presence of a small amount of the electrolyte. On persistent dialysis, the electrolyte is completely removed. As a result, the colloidal sol becomes unstable and gets coagulated.
11. The buildings blocks in the structure of zeolites are truncated octahedral (cubo-octahedra). This structure is called "β-cage" or "sodalite cage."
12. In expression $(x/m) = KP^{1/n}$
x = mass of adsorbate ; m = mass of adsorbent.
13. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$.
14. Substances such as metal, their sulphites, etc., which do not mix directly with the dispersion medium to form a colloidal sol.
15. This can be done by placing anhydrous $CaCl_2$ in the apparatus which absorbs the moisture.
16. Higher the critical temperature of a gas, greater the ease of liquefaction, *i.e.*, greater the van der Waals' forces of attraction and hence greater the adsorption.
17. During adsorption, there is always a decrease in surface energy which appears as heat.
$\therefore$ ΔH of adsorption is always –ve
and ΔS (entropy of the gas) is also –ve
and for a reaction to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be –ve.
18. (a)

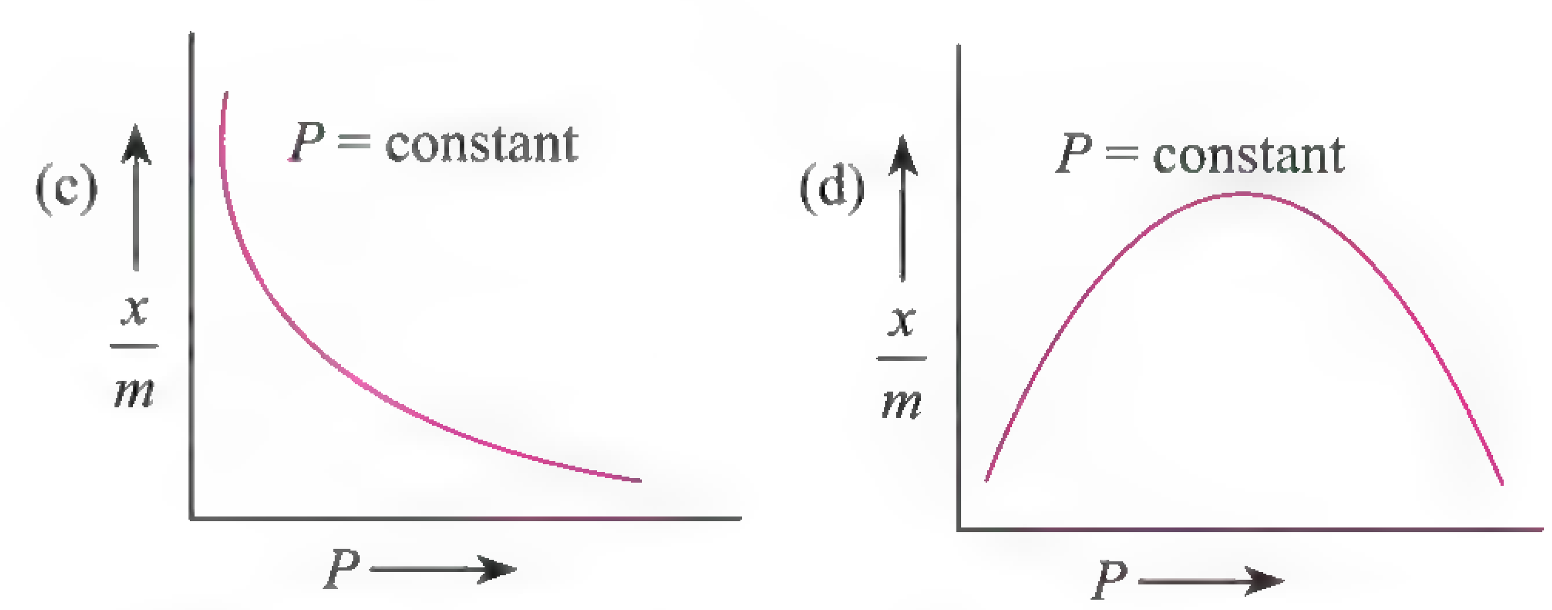


(b)



$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

(c) (d)



Physisorption Isobar Chemisorption Isobar

19. When gaseous molecules come in contact with the surface of a solid catalyst, a weak chemical bond is formed between the surface (catalyst) molecules and reactant (gas) molecules. Thus, concentration of reactant molecules increases at the surface.
The rate of reaction increases by adsorption of different molecules side by side facilitating the chemical reacton. Adsorption, being exothermic also help in increasing the rate of reaction (chemisorption increases with rise in temperature).
20. Diffusion of gas molecules occur at the surface of catalyst (solid) followed by adsorption. In the same way, the product formed diffuse from the surface of the catalyst leaving the surface free for more reactant molecules to get adsorbed and undergo reaction.
21. CMC of soap
10^{-4} M to 10^{-3} M
$x = 4$

22. Density of sites = 6.023×10^{14}

Total sites = $6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$

20% sites are occupied.

So, sites occupied = $\frac{20}{100} \times 6.023 \times 10^{17} = 12.04 \times 10^{16}$

$PV = nRT$

or $n = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 300} = 9.98 \times 10^{-9}$

Molecules = $9.98 \times 10^{-9} \times 6.023 \times 10^{23} = 6.02 \times 10^{16}$

Sites occupied per molecule of nitrogen is

$$\frac{\text{Number of sites}}{\text{Number of molecules}} = \frac{12.04 \times 10^{16}}{6.02 \times 10^{16}} = 2$$

23. Initial millimoles of $CH_3COOH = 100 \times 0.5 = 50$

Final millimoles of $CH_3COOH = 100 \times 0.49 = 49$

Millimoles adsorbed = 50 – 49 = 1

Moles adsorbed = $\frac{1}{1000}$

Molecules adsorbed = $\frac{1}{1000} \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$

Area per molecule = $\frac{\text{Total area}}{\text{Number of molecules}}$

$= \frac{3.01 \times 10^2}{6.023 \times 10^{20}}$

$= 5 \times 10^{19}\ m^2$

Exercises

Single Correct Answer Type

1. (1) **2.** (2) **3.** (1)

4. (4) Adsorption is an exothermic process.

5. (1)

6. (3) In sorption both adsorption and absorption take place.

7. (1) Adsorbent is a substance on which adsorption takes place.

8. (1) On increasing the temperature, adsorption decreases.

9. (2) **10.** (3) **11.** (1) **12.** (1)

13. (1) Hardness of water is due to carbonate or sulphate of Ca^{2+} and Mg^{2+} ions. When sodium aluminium silicate is added $Na^{\oplus}$ replaces Ca^{2+} and Mg^{2+} by adsorption, and hence water becomes soft.

14. (3) **15.** (1, 2) **16.** (3, 4) **17.** (3)

18. (2) $\frac{X}{m} \propto P^{1/n}$ or $\frac{X}{m} = KP^{1/n}$

Taking log on both sides,

$\log \frac{X}{m} = \log K + \frac{1}{n} \log P$

19. (4) Enthalpy of adsorption regarding physisorption is not positive. Rather it is negative.

20. (1) At high pressure,

$1 + bp \approx bp$

$\frac{x}{m} = \frac{ap}{bp} = \frac{a}{b}$

21. (1) At high pressure,

$\frac{x}{m} = \frac{ap}{1+bp}$ (and $1 + bp \approx bp$)

$= \frac{ap}{bp} = \frac{a}{b}$

22. (4) $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$

It is of the form $y = mx + c$.

Therefore, slope of the line will be $\frac{1}{n}$.

23. (4) CH_3COOH adsorbed = 0.5 – 0.49 = 0.01 M

No. of molecules adsorbed

$= 0.01 \times \frac{100}{1000} \times 6 \times 10^{23} = 6 \times 10^{20}$

Total area of charcoal = $2 \times 3 \times 10^2 = 600\ m^2$

$\Rightarrow$ area per molecule = $\frac{600}{6 \times 10^{20}} = 1 \times 10^{-18}\ m^2$

$= 1 \times 10^{-18} \times 10^4\ cm^2$

$= 1 \times 10^{-14}\ cm^2$

24. (3) Pressure of gas ∝ No. of gas molecules mass) striking the given area of surface of adsorbent.

25. (2) Graph A corresponds to monomolecular adsorption as postulated by Langmuir.

Graph C shows deviation from Langmuir model. The amount of adsorption keeps on rising with increase in pressure. This is attributed to the formation of additional layer of physically adsorbed gas molecules. For example, this graph is furnished by adsorption of nitrogen on an iron or a platinum catalyst at –195°C.

Graphs B and D have been observed in those cases in which there is possibility of condensation of gases in the minute capillary pores of the adsorbent at pressure even below the saturation pressure of the gas.

26. (3) When a diatomic gas adsorbs as atoms on the surface of a solid, the Langmuir adsorption isotherm becomes:

$$\theta = \frac{x}{m} = \frac{(kp)^{1/2}}{1+(kp)^{1/2}}$$

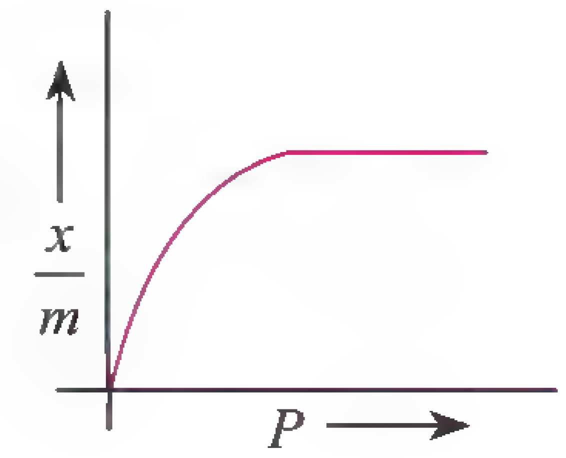
27. (2) Physical or van der Waals' adsorption is more pronounced at low temperature and high pressure.

28. (3) The gas which is easily liquefied undergoes greater extent of adsorption on the surface of adsorbent. Thus, greater is the critical temperature, more is the extent of adsorption.

	H_2	N_2	CH_4	CO_2
T_C	33 K	126 K	190 K	304 K

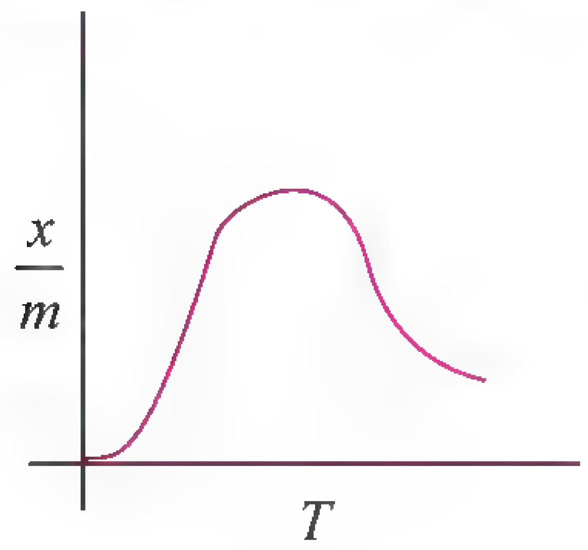
Thus, CO_2 will be the most adsorbed gas on the surface of activated charcoal.

29. (1)

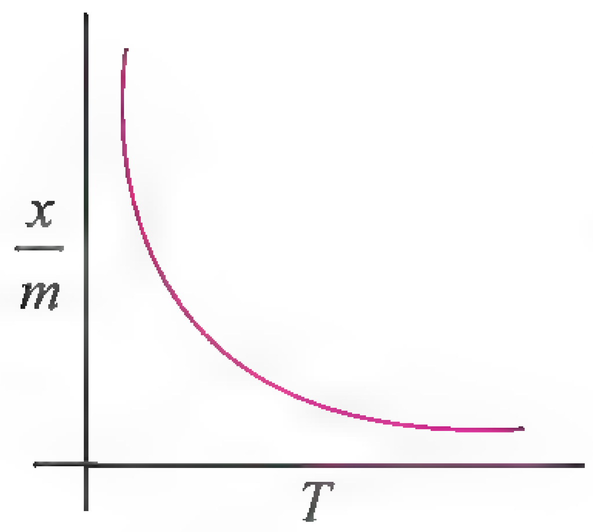


30. (4) Surface area↑ rate of adsorption↑

31. (3)



Chemical adsorption



Physical adsorption

32. (4) At 83 K physical adsorption takes place effectively so multimolecular layers formed.

33. (1) Temp↑ Extent of adsorption↓

34. (3) The potential difference that exists between the stationary layer of compensating charges and the diffuse layer (present is the body of the solution) is called zeta potential or electrokinetic potential.

35. (3) Blue colour of sky is due to scattering of light by dust particle (Tyndall effect).

36. (3)

37. (1) In fog, liquid water is dispersed in gas.

38. (1, 2)

39. (3) As_2S_3 sol is a negatively charged colloid. Al^{3+} has greater charge, therefore, $Al_2(SO_4)_3$ is most effective in the coagulation of As_2S_3 sol.

40. (4) $Al(OH)_3$ is positively charged sol. K_3PO_4 has greater negative charge. Hence, it is most effective in coagulation of $Al(OH)_3$ sol.

41. (2) **42. (3)**

43. (1) Refer text.

44. (2) **45. (3)** **46. (4)**

47. (2) Peptization is a process of passing of a precipitate into colloidal solution on the addition of electrolyte.

48. (2) Tyndall effect is observed for colloidal solution.

49. (2) Dialysis is a process of purifying a substance.

50. (1) **51. (3)** **52. (3)** **53. (1)**

54. (1) Due to scattering, smoke has blue tinge.

55. (1)

56. (1) **57. (2)**

58. (2) **59. (2)** **60. (1)**

61. (3) The reciprocal of gold number is directly proportional to the protecting power.

62. (4) Statement (4) is wrong.

Correct statement is: Above CMC, surfactant molecules undergo aggregation and micelles are formed.

Micelles are generally formed by the aggregation of several ions or molecules with lyophilic as well as lyophobic parts. They act as detergents, emulsifiers and dispersants. They are used in petroleum recovery.The cleansing action of soap is due to the fact that soap molecules form micelles around the oil droplets.

63. (4) Statement (4) is wrong:

Correct statement: High ratio of surface area to the volume. Colloidal state possesses lower surface tension or increase in surface area, due to which colloidal sol. acquires more adsorption power.

(3) Sodium is a highly reactive metal. It reacts exothermally with water and explodes.

64. (4) Statement (4) is incorrect.

Correct statement: Blood contains negatively charged particles.

(1) Smaller is the size, faster is motion.

(2) Continuous collisions of dispersed phase particles with dispersion medium gives irregular motion in sol. state.

(3) Black diamond is an impure form of polycrystalline diamond consisting of diamond, graphite, and amorphous carbon.

65. (4) Flocculating value of ion depends on both, the nature and magnitude of the charge of the flocculating ion.

66. (1) As_2S_3 is a negative colloid hence Al^{3+} will be most effective for its coagulation.

67. (4) $[AgI]Ag^{\oplus}$ will not be coagulated by the addition of $Ag^{\oplus}$ or $NO_3^{\ominus}$ ions.

68. (2) Number of milligrams of protective colloid added in 10 mL of colloidal gold to prevent its coagulation on addition of 1 mL of 10% NaCl solution is called gold number.

∴ Gold number of present colloidal substance = 25 (Gold number is usualy given in mg.)

69. (2) $[AgI]I^{\ominus}$ colloid will be formed only when the iodide ion is present in excess.

70. (2) $As_2S_3 + H_2S \longrightarrow As_2S_3 : S^{2-} : H^{\oplus}$

Preferential adsorption of S^{2-} takes place. So negative charge is developed.

71. (4) Sulphur solution is multimolecular by hydrophobic in nature.

72. (4) No stabilising agent required for the preparation of lyophilic sol.

73. (3) Coagulation value

$$= \frac{\text{Number of millimoles of electrolyte required}}{\text{Volume of colloidal solution (in litre)}}$$

$$= \frac{10 \times 0.5}{50} \times 1000 = 100$$

74. (2) Mass of acetic acid adsorbed by 2 g charcoal

$$= 100 \times 10^{-3} \times (0.6 - 0.5) \times 60$$

$$\Rightarrow 0.6;\ \frac{x}{m} = \frac{0.6}{2} \Rightarrow 0.3$$

75. (1, 3)

Catalyst decreases the activation energy for the reaction hence reaction speeds up. It also decreases entropy (more negative), therefore, free energy less positive or more spontaneous.

76. (2) Ni is used for catalytic hydrogenation of oil.

77. (2)

78. (1) Catalyst changes the activation energy (E_a).

79. (3)

80. (2) For polymerization of ethene, Fe and Co is used.

81. (4) **82. (1)**

83. (4) Statements (1), (2) and (3) are incorrect

Correct (1): Does not occur at the interface of phases,

Correct (2): Enzyme pepsin in stomach and trypysin in intestine

Correct (3): Convert alcohol to alkanes (petrol)

84. (1)

i. Reaction in which catalyst is in different phase than other (reactants and products) is known as heterogeneous catalysis.

ii. $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

Here, reactant SO_2 and product SO_3 are in gaseous phase while platinum is in solid phase. So, this reaction represents a heterogeneous catalysis.

iii. $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

Similarly, here N_2 and H_2 reactant are in gaseous are in gaseous phase while NH_3 is in solid phase. Whereas in other reactions catalyst is in same phase with reactant(s) and product(s).

85. (3) Such a process involving oxidation of one substance in presence of other which would otherwise not been possible is called induced catalysis or better to say induced oxidation.

86. (2) In absence of catalyst: Activation energy $(E_a) = z$

In presence of catalyst: Activation energy $(E_a') = p$

$\therefore$ decrease in energy of activation $= E_a - E_a' = z - p$

87. (2) Enzymes decrease the activation energy to greater extent.

88. (1) It is preferentially adsorb on the caalyst.

89. (1) Negative catalyst

90. (4) Enzyme are specific in nature.

91. (2) Smaller the gold number of protective colloid, greater is the protective power.

92. (4) Gold number $= \dfrac{6.0 \times 10^{-5} \times 10^3 (\text{mg}) \times 10}{20} = 0.03$

93. (3) As_2S_3 sol is negatively charged owing to preferential adsorption of S^{2-} ions. Cation would be the effective ion in coagulation.

Flocculating value = minimum milli mol of the effective ion per liter of sol $= \dfrac{4 \times 0.005 \times 10^3}{4 + 16} = 1.0$

94. (4) $SnO_2(s) + 2KOH(aq) \longrightarrow K_2SnO_3(aq) + H_2O$

SnO_2^{3-} ions would be preferentially adsorbed by SnO_2 particles.

Multiple Correct Answers Type

1. **(2, 3)**
2. **(1, 2)**

(3) is wrong because chemical adsorption first increases and then decreases with increase in temperature.

(4) is wrong because as a result of adsorption, there is a decrease in surface energy.

3. **(1, 2, 4)**

Physisorption does not require activation energy.

4. **(1, 2, 3)**

Particle size of an adsorbent affects the amount of adsorption.

5. **(1, 2, 4)**

In chemisorption, adsorption first increases and then decreases.

6. **(1, 2, 4)**
7. **(1, 2, 4)**

E_a is zero for physisorption and is positive for chemisorption.

8. **(1, 3)**

Statement (2) and (4) are wrong:

Correct (2): It forms multimolecular layer

Correct (4): Emulsifiers work on the principle of adsorption and adsorption is a surface phenomenon.

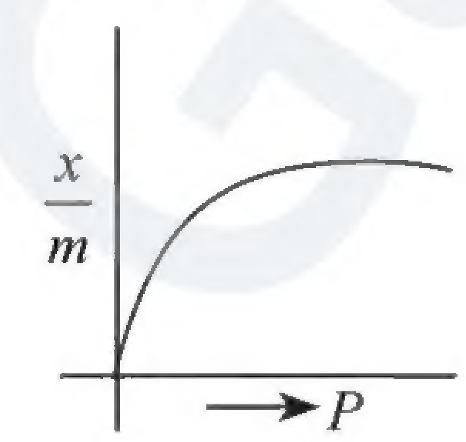
9. **(1, 2, 4)** are incorrect

(3) is correct: $\log \dfrac{x}{m} = \log K + \dfrac{1}{n} \times \log P$

10. **(1, 3, 4)** are correct.

(2) is incorrect: At point B $\dfrac{x}{m} \propto P^{1/n}$

11. **(1, 2, 3)**



12. **(1, 3, 4)**

Low temperature is favourable for physical adsorption.

Chemical adsorption requires activation energy.

13. **(1, 2, 3)**

Dust is an aerosol and not a solid sol.

14. **(1, 3, 4)**

Silicic acid is a non-elastic gel.

15. **(1, 4)**
16. **(1, 4)**

Milk is emulsion, butter is gel. Smoke and fog have gas (air) as the dispersion medium and hence are aerosol.

17. **(1, 2, 3)**
18. **(1, 2, 4)**

Smoke is an aerosol (solid carbon particles dispersed in air).

19. **(1, 2, 3)**

Gold sol is negatively charged. Hence, most effective for coagulation will be Mg^{2+} ions.

20. **(1, 4)**

Starch and cellulose are high molecular mass molecules.

21. **(1, 2, 3)** 22. **(1, 4)** 23. **(1, 3)**

24. **(1, 3, 4)**

Statement (1) is wrong.

Correct (1): Gel is a colloidal solution of liquid in solid.

25. **(1, 2, 4)**

Statement (3) is correct.

Correct (1): Maxwell distribution is not the property of colloidal solution. It is used for calculating particle speeds in idealized gases where the particles move freely inside a stationary container.

Correct (2): Peptisation is not used to destroy the emulsion

High-voltage electricity is an effective method of breaking emulsions. When an electric field is applied. The water molecules move rapidly and collide with each other and coalesce. Demulsification can also be done by heating or freezing.

Correct (4) Mechanical disintegration method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.

Therefore it is used to prepare colloidal graphite and printing ink. Thus statement (3) is correct.

26. (1, 3, 4)

A protective colloid is a colloidal substance that protects other colloids from getting coagulated in the presence of an electrolyte colloidal silica is not a protective colloid.

27. (2, 4)

Presence of equal and similar charges on colloidal particles provides stability to colloids as repulsive forces between charge particles having same charge prevent them from colliding when they come closer to each other.

28. (1, 2, 3)

(1) is wrong because zeolites are not used as such but are first heated in vacuum so that the water of hydration is lost.

(2) is wrong , because enzyme have maximum activity at pH of 7.4

(3) is wrong because enzyme has maximum activity at 37°C.

29. (1, 2, 4)

A catalyst is a substance that may increase or decrease the speed of reaction, also it may be added from outside and sometimes may produced during the reaction.

30. (1, 2, 3)

Cellulose is not an enzyme.

31. (1, 2, 4)

32. (2, 3, 4)

Catalyst does not change equilibrium.

33. (1, 3, 4)

34. (1, 3, 4)

Efficiency of catalyst depends upon the number of free valencies.

35. (1, 2, 3)

36. (1, 3)

Explanation (1): catalyst provides a new path for the reaction in which a activated intermediate complex of lower potential energy is formed.

Statements (2) and (4) are wrong:

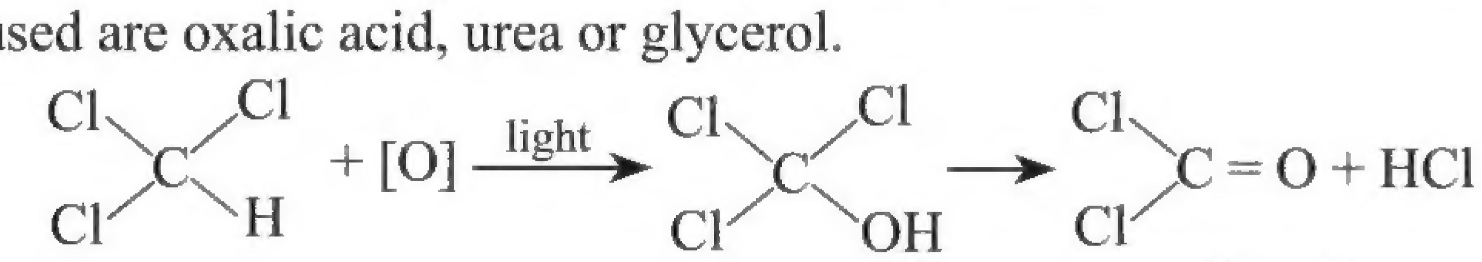
Correct (2): catalyst changes physically and qualitatively as it is unaltered during the reaction and remain quantitatively intact after completion of reaction and chemically does not change.

Correct (4): Acetamide acts as inhibitor

37. (1, 2, 3)

An antiknock agent is a gasoline additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs. Tetraethyl lead is still in use as a high octane additive.

H_2O_2 decomposes to H_2O and O_2 in presence of light. That's why it is stored in dark glass bottles for this reaction. The inhibitors used are oxalic acid, urea or glycerol.



(Phosgene)
Highly poisonous

To convert phosgene to ethyl carbonate and to retard the oxidation 1% ethyl alcohol is used.

$$COCl_2 + C_2H_5OH \longrightarrow (C_2H_5)_2CO + 2HCl$$

38. (1, 2)

(1) Same reactants may give different products by using different catalysts as different catalysts have different specific functions to mold the reaction towards specific product. *e.g.*, starting with H_2 and CO, and using different catalysts, we get different products.

i. $CO(g) + 3H_2 \xrightarrow{Ni} CH_4(g) + H_2O(g)$

ii. $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO} CH_3OH(g)$

iii. $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

(2) Catalyst does not change ΔH of reaction as ΔH of reaction is difference between enthalpy of reactants and products. So, it does not change during catalysed reaction.

Linked Comprehension Type

Paragraph 1

1. **(1)** Adsorption is always exothermic.
2. **(1, 2, 3)** All except (4) are linear.
3. **(3)** The critical temperature of the given gases is in the order: $SO_2 > NH_3 > HCl > CO_2$. Hence, their adsorption is in the same order.
4. **(2)** Solute is adsorbed from concentrated KCl solution whereas solvent (water) is adsorbed from dilute KCl solution.

Paragraph 2

5. (4) **6. (2, 3)** **7. (1)** **8. (1)** **9. (1)**

Paragraph 3

10. (1) **11. (1)** **12. (1, 2)** **13. (3)**
14. (1)

Matrix Match Type

1. (a → s) Peptization is a process of conversion of a freshly precipitated substances into colloidal sol by shaking with suitable electrolyte.

(b → r) Flocculation is minimum numbers of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal sol.

(c → p) Blood is a natural colloid.

2. (a → r) Gold number is the minimum number of milligrams of a lyophilic sol, needed to protect 10 mL of gold sol by addition of 1 mL of 10% NaCl.

3. (c → t) Dialysis is the purification of colloids.

4. (a → q; b → r; c → s; d → t; e → u; f → p)

5. (d → p) Gas mask works on the principle of adsorption.

6. (c → q, r) Activated adsorption requires high temperature.

7. (b → s) In adsorption, molecules of substances are accumulated in bulk also.

Numerical Value Type

1. **(3)** Haemoglobin is positively charged sol. Hence the sol with negative charge can coagulate haemoglobin, i.e., starch, clay, As_2S_3, CdS.

2. **(1)** Silicic acid is negatively charged sol. Hence the sol with positive charge can coagulate silicic acid, i.e., $Fe(OH)_3$, $Ca(OH)_2$, $Al(OH)_3$, basic dye.

3. **(4)** 2 mL of 1 M NaCl contains NaCl = $\frac{2}{1000}$ = 2 mmol

   Thus 500 mL of As_2S_3 sol require NaCl for complete coagulation = 2 mmol

   Hence 1 L, i.e., 1000 mL of the sol require NaCl for complete coagulation = 4 mmol

   Therefore, flocculation value of NaCl = 4.

4. **(3)** Haemoglobin added to 100 mL of gold sol to prevent coagulation by 1 mL of 10% NaCl sol = 0.03 g = 30 mg

   haemoglobin required to be added to 10 mL of gold sol to prevent coagulation by 1 mL of 10% NaCl sol = 3 mg.
   Therefore, gold number of haemoglobin = 3.

5. **(2)** Gold number of gelatin = 0.01

   or 0.01 mg gelatin required to be added to 10 mL of gold sol to completely prevent coagulation of 1 mL of 10% NaCl solution.

   Therefore gelatin added to 1000 mL of gold sol to prevent coagulation = $\frac{0.01\times1000}{10}$ = 1 mg.

6. **(4)** Mass of HCl acid adsorbed by 10 g charcoal

   $= 526.3 \times 10^{-3}(0.5-0.4)\times 38 \approx 2$ (Mw of HCl = 38 g mol^{-1})

   The amount of adsorption

   $\frac{x}{m} = \frac{2}{0.5} = 4$

7. **(1)** As_2S_3 sol is negatively charged owing to preferential adsorption of S^{2-} ions. Cation would be effective ion in coagulation.

   Flocculating value = millimole of the effective ion per litre of sol

   $= \frac{5\times0.006\times10^3}{5+10} = 2$

8. **(3)** $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$

   $\therefore$ Plot of $\log\frac{x}{m}$ versus $\log P$ is linear with slope = $\frac{1}{n}$ and intercept = $\log K$

   Thus $\frac{1}{n} = \tan\theta = \tan 45° = 1$ or $n = 1$

   $\log K = 0.301$ or K = antilog 0.301 = 2

   At P = 3 atm

   $\frac{x}{m} = KP^{1/n} = 2\times(3)^1 = 6$

Archives

JEE Advanced

Single Correct Answer Type

1. **(3)** Sb_2S_3 solution is a negatively charged solution. The process by means of which the particles of the dispersed phase in a solution are precipitated is known as coagulation or flocculation. An ion having an opposite charge to that of the solution is responsible for coagulation. This ion is thus known as active ion. The coagulating or flocculating power of the active ion increases with the valency of the active ion. Greater the valency of the active ion, greater is its power to cause coagulation. This is known as Hardy Schulze rule. For a negatively charged solution,

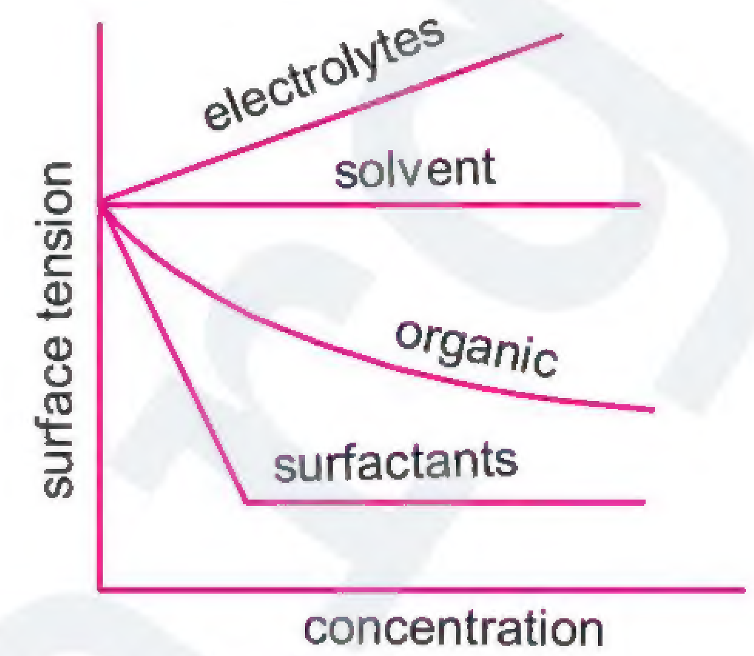
   $Al^{3+} > Ca^{2+} > Na^{\oplus} = NH_4^{\oplus}$

2. **(1)** As_2S_3 is an anionic sol (negative sol) hence coagulation will depend upon coagulating power of cation which is directly proportional to the valency of cation (Hardy-Schulze rule).

3. **(2)** Adsorption of methylene blue on activated charcoal is physical adsorption hence it is characterized by decrease in enthalpy.

   Hence (2) is correct.

4. **(4)** Strong electrolytes like KCl increase the surface tension slightly. Low molar mass organic compounds usually decrease the surface tension. Surface active organic compounds like detergents sharply decrease surface tension.



5. **(2)** As the concentration increases beyond CMC, stearate ions get asociated and form micelles. Thus causes the concentration of the anions to decrease and causes decrease in Λ_m after CMC.

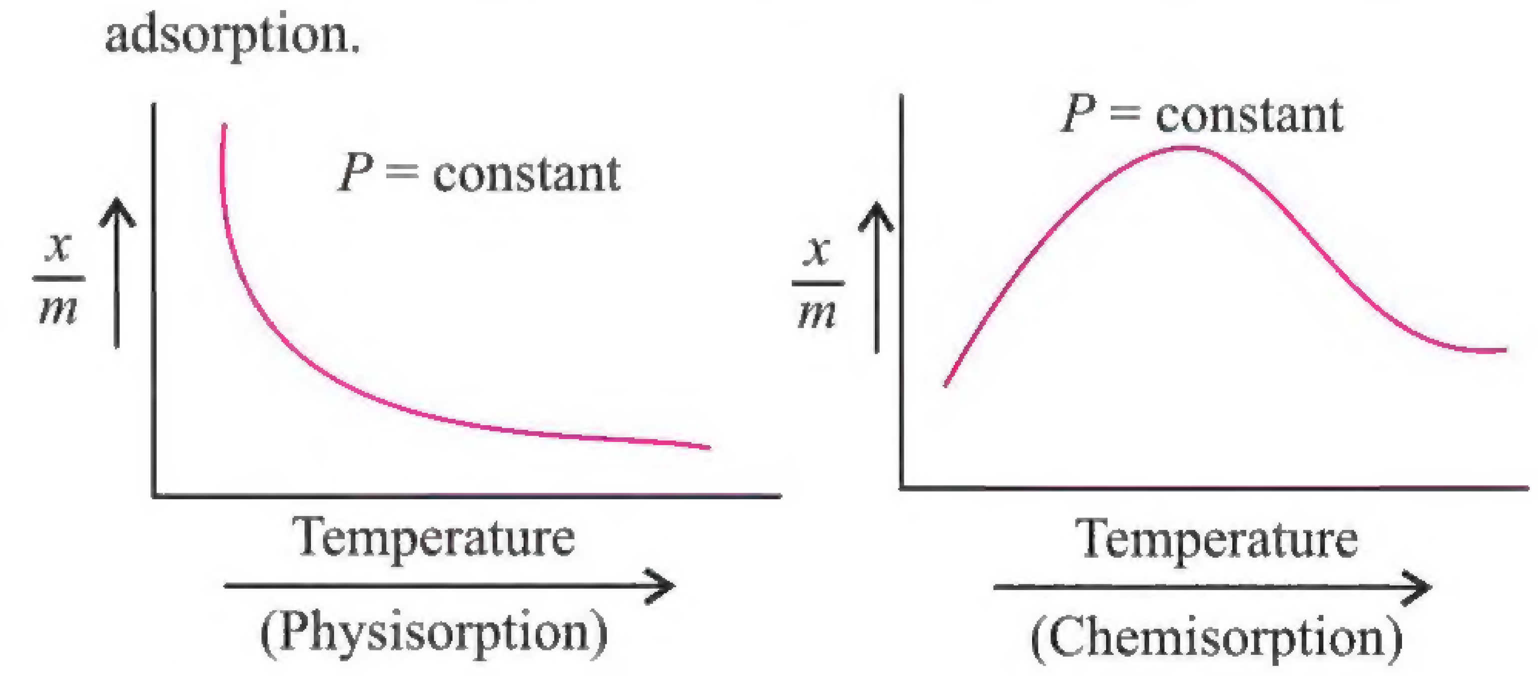
Multiple Correct Answers Type

1. **(1, 2, 4)**

   (1) Adsorption is always exothermic (factual statement).

   (2) It is also a factual statement.

   (3) The statement is wrong. Physisorption decreases with increase in temperature. But chemisorption first increases with increase in temperature and then decreases. The effect is called activated adsorption.



   (4) It is a factual statement.

2. **(1, 4)**

   (1) due to preferential adsorption of common ions

   (2) False

   (3) False (due to repulsion not due to attraction)

   (4) The layer of oppositely charged particles around any colloidal particles will decrease the potential energy of system as a whole.

3. **(1, 3)**

   In physisorption on increasing temperature at constant pressure, adsorption decreases while in chemical adsorption on increasng temperature due to requirement of activation energy adsorption will increase at same pressure. So, I is physisorption while II is chemisorption.

   III is physical adsorption as on increasing temperature. extent of adsorption is decreasing.

   IV is representing enthalpy change (which is high) during chemical adsorption (due to bond formation). So, IV is valid for chemical adsorption. So, answer is (1) aud (3).

4. (2, 4)

[Statements (2) and (4) are correct]

In adsorption process both ΔH & ΔS is –ve. Higher the critical temperature of a gas higher the extent of adsorption.

Cloud is not an emulsion. [Statement (1) is wrong]

Brownian motion depends on the size of the particles.

[Statement (3) is also wrong].

5. (2, 3)

(1) Peptization is a method of formation of colloidal solution by which precipitates are converted into colloidal solution.

(2) In colloidal solution, if concentration is same, so ΔT_f is same and hence, freezing point is same also.

(4) Micelles are multimolecular

Surfactants form micelle above critical micelle concentration (CMC) which depends on temperature.